

Condensed Matter

The staff consists of 21 professionals and 2 technicians, plus a variable number of undergraduate and graduate students (at present: 20)

Projects on the move, all of them on solid state physics or condensed matter in general, include a variety of topics and techniques, with an important thematic inbreeding linking them. A brief description of the intervening Groups and Laboratories follows.

Laboratory Of Chemical Synthesis And Characterization:

A variety of perovskitic materials are obtained and characterized, in particular substituted manganese oxides. Among other materials of interest we find copper and alkaline earth metals, anhydrous formates, mixed copper and transition metals hydrated formates, and other related compounds of biological or technological interest. In this area some hydroxyapatites as well as their cationic and anionic substitution derivatives are also studied.

X-Ray Diffraction:

Areas of interest are: molecular structures of new coordination compounds with transition metals and polymorphs with a pharmacological interest, structural phase transitions and the study of compounds with modulated structures. Present interest is centered in the study of manganese oxides structure by Rietveld refinement. The Laboratory runs a facility for the identification of third party crystalline samples by x-ray powder diffractometry.

Raman Spectroscopy:

Systematic studies are performed on thin films of amorphous carbon (diamond like) over different substrates, in order to fully characterize them.

Mössbauer Spectroscopy:

⁵⁷Fe Mössbauer spectroscopy is at present applied to the study of: nanoparticles -mainly nanohematites-, the mineralogy of argentine soils and Zr-containing alloys. Some works of corrosion of steels were also performed.

Electrical Properties:

Measurements of dielectric constants, electrical conductivity and alternate magnetic susceptibility are performed on ceramics and single crystals, as a function of temperature (30-300 K), in the presence of a magnetic field of up to 1 Tesla. Presently, the interest is centered on the study of manganese oxides with magnetoresistent properties.

Condensed Matter Theory:

The different lines include: calculations of electronic structures and magnetic properties of different metallic systems of low dimensionality through 'ab-initio' methods (LMTO-FLAPW). Calculation of transport properties on disordered systems and metallic superlattices. Dynamical properties of molecular crystals, using molecular dynamics. Static and dynamic properties of incommensurate phases. Molecular dynamics applied to C60-like molecules. Montecarlo calculations to obtain the phase diagram and dielectric constant of dipolar molecular liquids and antiferromagnetic systems with defects. Extended dynamical systems with self-criticality, complex systems, game theory. Study of the liquid-solid transition, from the point of view of a broken translation symmetry in a liquid. Order-disorder phase transitions in periodic systems with competing interactions. Structural and dynamical properties of C and Si compounds using semiempirical potentials.

“On the Metallic Behavior of Co Clusters”

*F.Aguilera-Granja, J.M. Montejano-Carrizales,
J.Guevara and A.M.Llois*

Solid State Comm. 113 (2000) 147

The role of structure in the nonmetal-metal transition of Co clusters is investigated by performing calculations for different symmetries : hexahedral, octahedral and decahedral. This transition occurs when the density of states at the Fermi level exceeds $1/kT$ and the discrete energy levels begin to form a quasi-continuous band. The electronic structure is calculated including spd orbitals and spillover effects in a Hubbard Hamiltonian solved within the unrestricted Hartree-Fock approximation. We find that in small clusters ($N < 40$) the metallic behavior is strongly related to the geometrical structure of the cluster. We compare our results with those coming out of a simple Friedel's model.

“Calculation of the Magnetoresistance of YMn_2Ge_2 and $LaMn_2Ge_2$ ”

J. Milano and A.M. Llois

Physica Status Solidi B220 (2000) 409

We have calculated the diffusive conductivity and ballistic conductance of the layered compounds YMn_2Ge_2 and $LaMn_2Ge_2$. For YMn_2Ge_2 we obtain a negative band contribution to the giant magnetoresistance. For $LaMn_2Ge_2$ we show that the band contribution can already explain the experimentally observed large positive magnetoresistance if a nearly ferromagnetic structure is considered.

“Electronic Properties of small free Co-clusters”

*F. Aguilera Granja, J.M. Montejano Carrizales,
J.A. Guevara and A.M. Llois*

Physica Status Solidi B220 (2000) 455

We present a systematic study of the average magnetic moments and the non-metal-metal transitions of free Co_N clusters having different geometries: hexahedral, octahedral and decahedral. The electronic structure is calculated with a parameterized Hubbard Hamiltonian with spd electrons within the unrestricted Hartree-Fock approximation, and spill-over effects are considered. We compare our calculations with other theoretical calculations in the literature. We also comment on the experimental results.

“Linear defects on Cu(111): The appearance and disappearance of surface states”

M.A. Barral and A.M. Llois

Phys. Rev. B62 (2000) 12668

The appearance and disappearance of the Schockley surface state at Cu(111) is studied as a function of density and width of extended adsorbed defects using a Hamiltonian which contains s, p and d orbitals in the basis. The local electronic density of the surface state at the Γ point is obtained atom by atom. We also report on 1D and 2D defect states lying near the Fermi level.

“Study of Ce Intermetallic Compounds: A Local-Density Approximation, Classification and Hybridization Effects”

V. Vildosola and A.M. Llois

Phys. Rev. B62 (2000) 7027

Spin-polarized calculations within the local-density approximation have been made with the goal of characterizing Ce intermetallic compounds. Effects of symmetry and chemical environment on 4f hybridization and, thereafter, on magnetization have been studied.

“New Superhard Phases for Three-Dimensional C60-based Fullerites”

E. Burgos, E. Halac, R. Weht, H. Bonadeo, E. Artacho and P.Ordejon

Physical Review Letters 85 (2000) 2328

We have explored new possible phases of 3D C60-based fullerites using semiempirical potentials and ab-initio density functional methods. We have found three closely related structures - two body centered orthorhombic and one body centered cubic - having 52, 56 and 60 tetracoordinated atoms per molecule. These 3D polymers result in semiconductors with bulk moduli near 300 GPa, and shear moduli around 240 GPa, which make them good candidates for new low density superhard materials.

“On the Crystal Structure of C₃₆”

E. Burgos, E. Halac, H. Bonadeo

Chem. Phys. Lett. 320 (2000) 14

We present calculations which indicate that the newly synthesized C₃₆ molecule probably forms a Van der Waals crystal, of rhombohedral or hexagonal structure. Our results, based on intermolecular potentials of the atom-atom form, are in good agreement with the existing experimental evidence. Using covalent semiempirical potentials, we find that if molecules are placed closely together they tend to form extra bonds, several energy minima are thus obtained, but these correspond to structures with either too large or too short intermolecular distances in the basal plane.

“Electronic Structure of the Superconducting Layered Ternary Nitrides CaTaN₂ and CaNbN₂”

J.M. Oliva, R. Weht, P. Ordejon and E. Canadell

Phys. Rev. B62 (2000) 1512

The electronic structure of the layered ternary nitrides CaMN₂ (M=Ta, Nb) has been studied and the results are compared with those for the related LiMoN₂ phase. It is shown that the former are two-dimensional metals, with a Fermi surface very similar to that of the 1T-TaX₂ (X = S, Se) dichalcogenides, whereas the latter is a three-dimensional metal. The three phases show strong covalent bonding within the layers but ionic bonding with the alkali atom sheets.

“Electronic Fine Structure on the Electron-Hole Plasma in SrB₆”

C.O. Rodriguez, R. Weht and W.E. Pickett

Physical Review Letters 84 (2000) 3903

Fine structure arising from the mixing between overlapping electron and hole bands in alkaline earth hexaborides such as SrB₆ leads to lower energy (temperature) scales than occurs in their doped counterparts (viz. Sr_{0.995}La_{0.005}B₆), which are high critical temperature, tiny moment ferromagnets. Two of the calculated Fermi surface extremal orbits agree well with two of the three observed miniscule cross sections, and optical absorption and transport behavior are consistent with calculated energy scale. These results suggest that SrB₆ is a conventional Fermi liquid at the temperature of the de Haas -- van Alphen measurements, but the drop in resistivity at 0.5 K likely indicates a phase transition to a more conductive phase.

“Self-organization in a minority game: the role of memory and a probabilistic approach”

E. Burgos and H. Ceva.

Physica A 284 (2000) 489

A minority game whose strategies are given by probabilities p , is replaced by a ‘simplified’ version that makes no use of memories at all. Numerical results show that the corresponding distribution functions are indistinguishable. A related approach, using as random walk formulation, allows us to identify the origin of correlations and self

organization in the model, and to understand their disappearance for a different strategy's update rules, as pointed out in a previous work.

“The ordered and orientationally disordered crystalline phases of the flexible C₄F₈ molecule”

Z. Gamba and B. M. Powell

J. Chem. Phys. **112** (2000) 3787

There is ample experimental evidence for the existence of several crystalline phases of C₄F₈, although they still have been not clearly identified. In this paper we report a series of molecular dynamics (MD) simulations using a partially flexible molecular model, which takes into account the mixing of the low frequency intramolecular modes and lattice modes. The calculations are carried out at constant pressure and constant temperature and the algorithm employed allows for volume and symmetry changes of the (MD) sample as a function of thermodynamic variables. Although several stable crystalline phases are found, their number is still less than determined by experiments.

“Test of a simple and flexible molecule model for α -, β - and γ -S₈ crystals”

C. Pastorino and Z. Gamba

J. Chem. Phys. **112** (2000) 282

S₈ is the most stable compound of elemental sulfur in solid and liquid phases, at ambient pressure and below 400K. Three crystalline phases of S₈ have been clearly identified in this range of thermodynamic parameters, although no calculation of its phase diagram has been performed yet. α - and γ -S₈ are orientationally ordered crystals while β -S₈ is measured as orientationally disordered. In this paper we analyze the phase diagram of S₈ crystals, as given by a simple and flexible molecule model, via a series of molecular dynamics (MD) simulations. The calculations are performed in the constant pressure- constant temperature ensemble, using an algorithm that is able to reproduce structural phase transitions.

“Test of a simple and flexible S₈ model molecule in α -S₈ crystals”

C. Pastorino and Z. Gamba

Chem. Phys. Lett. **319**, 20 (2000).

α -S₈ is the most stable crystalline form, at ambient pressure and temperature (STP), of elemental sulfur. In this paper we analyze the zero pressure low temperature part of the phase diagram of this crystal, in order to test a simple and flexible model molecule. The calculations consist in a series of molecular dynamics (MD) simulations, performed in the constant pressure- constant temperature ensemble. Our calculations show that this model, that gives good results for three crystalline phases at STP and T._>300K, fails at low temperatures, predicting a structural phase transition at 200K where there could be none.

“Study of sulfur α -S₈ crystals with an anisotropic intermolecular potential model”

C. Pastorino and Z. Gamba

Chem. Phys. **261**, 317 (2000)

An anisotropic atom-atom intermolecular potential model is used to study the α - S₈ phase of this elemental sulfur compound. Comparisons with the results obtained in previous papers, using an isotropic model are performed. The possible existence of a monoclinic α' -S₈ polymorph is discussed.

“Density fluctuations and entropy”

J.A. Hernando and L. Blum,

Phys. Rev. E **62**, 6577 (2000)

A new functional for the entropy that is asymptotically correct both in the high and low density limits is proposed. The new form is

$$S = S^{(id)} + S^{(ln)} + S^{(r)} + S^{(c)}$$

where the new term $S^{(c)}$ depends on the p-bodies density fluctuations α_p and renormalizes the ring approximation $S^{(r)}$. This result is obtained by analyzing the functional dependence of the most general expression of the entropy: Two main results for $S^{(c)}$ are proven: i) In the thermodynamic limit it is only a functional of the one body distribution function and ii) by summing to infinite order the leading contributions in the density a new numerical expression for the entropy with a new renormalized ring approximation is obtained. The relation of

these results to the incompressible approximation for the entropy is discussed and preliminary numerical results on hard spheres are presented.

“Structural and transport properties of La_{0.67}Sr_{0.33}Mn(1-x)Sn_xO₃ thin films”

S. Duhalde, M. Villafuerte, M.C. Tezzoli, G. Polla, A.G. Leyva, L. Correr

Applied Physics A69 (7) (2000) 65

The magnetotransport properties of perovskite manganite films have attracted much recent interest because of the colossal magnetoresistance exhibited (CMR). The La_{1-x}Sr_xMnO₃ mixed valence compound contains Mn³⁺ with the configuration t_{2g}³ e_g¹ and Mn⁴⁺ ions with a t_{2g}³ structure. The doping with Sn could play a role regarding the structural and magnetotransport properties as the tin ions does not share the same interaction as the manganese ions. We report in this work the structural and transport characteristics of as-deposited and post-deposition annealed La_{0.67}Sr_{0.33}Mn_{1-x}Sn_xO₃ thin films by pulsed laser deposition (PLD). We analyzed the influence of the tin doping on films properties. X-ray diffraction (XRD), scanning electron microscopy (SEM) and R vs. T measurements were performed. We found that tin doping promotes oxygenation of the films, increasing the temperature of electrical transition T_c, and could be an alternative to post-annealing treatments.

“Pathological Mineralizations: Calcifications and Si-bearing particles in soft tissues and their eventual relationship to different prostheses”

A.G. Leyva, S.L. Maghid, M.A. Rodríguez de Benyacar, M.A. Lazaro, J. Maldonado Cocco and G. Citera

Artificial Organs 24 (3) (2000) 179

Polarizing microscopy (PM), scanning electron microscopy (SEM), x-ray dispersive analysis (EDAX), x-ray diffraction (XRD), and infrared spectrometry (IR) were used to study the following pathological mineralizations: calcifications and silicon (Si)-bearing particles in cerebral tissue from an epileptic child; traces of Si-bearing particles in periprosthetic mammarian tissue, and calcifications in capsular mammarian tissue from a patient with a silicone gel mammarian implant, and 2 calcium-bearing compounds, atypical apatitic calcification, and a nonphosphorous-bearing calcification in

arterial tissues. In this tissue we also found Si-bearing particles due to an artifact from glassware.

“The monoclinic/orthorhombic phase transition in Ba₂Cu(HCOO)₆: an optical and X-ray powder diffraction study”

G. Polla, D. Vega, A.G. Leyva, P.K. de Perazzo, H. Lanza, M.A.R.de Benyacar

Phase Transitions, Vol. 72 (2000) 15

α -Ba₂Cu(HCOO)₆ grown at room temperature crystallizes in space group P2₁. On heating a reversible, hysteretic, equitranslational, first-order phase transition at about 60-90 °C takes place. Here we discuss the influence of thermal treatments on the occurrence, coexistence and stability ranges of the observed phases, as studied by several techniques (optical microscopy, differential scanning calorimetry and X-ray diffraction). On cooling a single set of domain walls parallel to (001) have been observed. Taking into account experimental results and the crystal pseudosymmetry of the α phase we propose that the high-temperature β phase crystallizes in space group Pbnm.

“Vibrational spectra of Ba₂Cu(HCOO)₆ crystals”

A. Ayala, J. Henriques Nieto, C. Paschoal, I. Guedes, J.M. Sasaki, P. Freire, F. Melo, J. Mendes Filho, A.G. Leyva, G. Polla, D. Vega, P. Perazzo

J.Raman Spectroscopy 31 (6) (2000) 491

Polarized Raman spectra of single crystals of barium copper formate at room temperature were recorded and analyzed. The spectra were obtained for geometries allowing the observation of A (TO) and B (TO and LO) species. The assignment of the fundamental modes was performed on the basis of formate group vibrations and correlations with previous data reported for other formate crystals. The observation of four separate wavenumbers for all internal modes of formate ion is indicative of four crystallographically non-equivalent formate ions in the unit cell.

“Controlled Phase Separation in La_{0.5}Ca_{0.5}MnO₃”

P. Levy, F. Parisi, G. Polla, D. Vega, G. Leyva, H. Lanza, R.S. Freitas and L. Ghivelder

Phys. Rev. B62 (2000) 6437

The ground state of the half doped manganite La_{0.5}Ca_{0.5}MnO₃ has a complex behavior, in which an antiferromagnetic charge ordered (AFM-CO) phase and a ferromagnetic (FM) phase can coexist. A systematic study of phase separation effects in polycrystalline La_{0.5}Ca_{0.5}MnO₃ under different thermal treatments is reported. Samples with average grain size ranging from 200 to 1300 nm were studied. Magnetic and electrical measurements show quantitative differences among samples in their low temperature behavior, indicating that the fraction of the FM phase gradually decreases as the grain size increases. Percolation of the FM phase in samples with even a small fraction of this phase suggests that grain boundaries play a distinctive role in the spatial distribution of coexisting phases. The defective structure at the grain surface could explain the local inhibition of the AFMCO phase, an effect that is gradually removed by grain size increase. Qualitative agreement of the data with this description is found. Besides, this effect is also found to be highly dependent on the oxygen content and its spatial distribution.

“Speciation of As(III) and As(V) in aqueous solutions using baker's yeast and hydride generation inductively coupled plasma atomic emission spectrometric determination”

P. Smichowski, J. Marrero, A. Ledesma, G. Polla and D. Batistoni.

Journal of Analytical Atomic Spectrometry (JAAS) 15 (2000) 1493

In this study, the use of *Saccharomyces cerevisiae* was evaluated as substrate for the biosorption of As(III) in the presence of As(V) from aqueous solutions. Experiments were performed in batch as a suitable and simple method to obtain information of arsenic uptake by yeast cells. The effect of chemical and physical variables affecting the biosorption of As were evaluated in order to select the optimal analytical conditions for the selective As retention by *Saccharomyces cerevisiae*. The parameters studied were: reaction media, pH, amount of biomass, analyte concentration and contact time. The influence of some concomitant ions up to 50 mg l⁻¹ was also tested. Quantitative determinations of As species in yeast and

supernatant were carried out by means of inductively coupled plasma atomic emission spectrometry with hydride generation. During all the steps of the optimisation process, As(V) remained in solution while As(III) was accumulated by the yeast cells. The speciation of inorganic As species in different kinds of natural waters was performed following the method proposed. Spiked water samples were also prepared and the recoveries in each phase were in all cases between 91 and 105%.

“Temperature dependent Raman study of CaCu(HCOO)₄ and Ca₂Cu(HCOO)₆ crystals”

C.W.A. Paschoal, M.R. Moura, A.P. Ayala, J.M. Sasaki, P.T.C. Freire, F.E.A. Melo, J. Mendes Fille, I. Guedes, A.G. Leyva, G. Polla, D. Vega and P.K. Perazzo

J. Solid State Chem. 8791 (2000) 338

Unpolarized Raman spectra of polycrystalline samples of calcium(II) copper(II) formate and dicalcium(II)copper(II)formate were recorded and analyzed in the temperature range from 30 to 300K. The observed modes at 300K were assigned on the basis of formate group vibrations and correlations with previous data reported for other formate compounds. The splitting of the internal HCOO modes agrees with the group theory predictions. No changes either in the wavenumber or intensity of Raman modes were observed when the temperature of the samples was cooled to 30K. This indicates that these compounds do not exhibit any phase transformation in the temperature range investigated.

“1-2-(Dimethylamino)-1-(4-methoxyphenyl) ethylcyclohexanol hydrochloride (Venlafaxine Hydrochloride)”

D. Vega, D. Fernández, G. Echeverría

Acta Cryst. C56 (2000) 1009

The crystal structure of racemic Venlafaxine hydrochloride (C₁₇H₂₈NO₂⁺, Cl⁻) consists of two types of parallel chains formed by translated Venlafaxine+cations, H-bonded by Cl⁻ anions, and characterized by the opposite chirality of their constituent molecules. These chains organize in two different types of broad layers of opposite handedness, related by a glide plane.

“Bis[chlorobis(1,10-phenanthroline-N,N’)](thiourea-S)nickel(II)Chloride Nitrate Diethanol solvate”

L. Suescun, A.W. Mombrú, R. A. Mariezcurrena, H. Pardo, S. Russi and R. Baggio

Acta Cryst. C56 (2000) 179

$C_{27}H_{26}Cl_{11.5}N_{6.5}NiO_{2.5}S$ crystallizes in the polar space group Fdd2 with 16 formulas per unit cell. The crystal structure is formed by cations of $[Ni(phen)_2(thiourea)Cl]^+$, chloride and nitrate counter ions and ethanol solvate molecules. The nickel atom is octahedrally coordinated to two bidentate phen, a monodentate thiourea and to a chlorine ion. Both the chloride and nitrate anions, which provide to the charge balance, are placed at special positions in a two fold symmetry axis. Hydrogen bonds play a key role in packing and conformation of the cation, determining a three-dimensional network.

“Triaqua-tris(m-oxodiacetato)di-praseodimium(iii) Pentahydrate and Hexaqua-tris(m-oxodiacetato) di-neodimium(iii) Dihydrate,oxodiacetic acid solvate”

R. Baggio, M.T. Garland, M. Perec

Acta Cryst. C56 (2000) 312

Two new complexes of the $Ln_2(oda)_3.nH_2O$ series are reported: $[Pr_2(C_4H_4O_5)_3(H_2O)_3.5H_2O]_n$ and $Nd_2(C_4H_4O_5)_3(H_2O)_6.2H_2O.C_4H_6O_5]_n$. The former is isostructural to the reported La compound while the latter is a new structural variety within the series. Each compound exhibits two independent, nine coordinated Ln centers showing a variety of coordination geometries.

“Tris(2,2’-Bipyridyl)-nickel(ii) thiosulfate, heptahydrate”

E. Freire, S. Baggio, A. Mombru, R. Baggio

Acta Cryst. C56 (2000) 541

The structure of the title compound ($C_{30}H_{38}N_6NiO_{10}S_2$) consists of monomeric $Ni(bipy)_3^{2+}$ cations embedded into an anionic network made up of $S_2O_3^{2-}$ ions and hydration water molecules. The structure presents the unusual feature of two neighbouring thiosulfates approaching linearly head to head to an unusually short S...S contact of 3.25 Å.

“Novel Europium and Gadolinium Compounds in the Lanthanide(III) Oxydiacetate Series”

P.F. Aramendia, R. Baggio, M.T. Garland, M. Perec

Inorg.Chim.Acta 303/2 (2000) 306

The preparation and characterization of the europium(III) and gadolinium(III) oxydiacetate compounds $\{[Ln_2(oda)_3(H_2O)_2].5H_2O\}_n$ are described. The crystallographic data reveal a novel structural modification within the lanthanide oxydiacetate series. Also, the first species of a lanthanide(III) containing oda and Hoda simultaneously, $[Eu(oda)(Hoda)(H_2O)].2H_2O$, is reported.

“Three New Zn(II) Sulfate Complexes”

M. Harvey, S. Baggio, A. Mombro and R.F. Baggio
Acta Cryst. C56 (2000) 771

The three zinc sulfate complexes presented herein display three completely different coordination modes, viz.: $Zn(C_{12}H_8N_2)(SO_4)(H_2O)_3 \cdot (H_2O)$ (octahedral, monomeric); $(Zn_2(C_{14}H_{12}N_2)_2(SO_4)_2)$ (tetrahedral, dimeric) and $[Zn(C_{10}H_8N_2)(SO_4)(H_2O)_2]_n$ (octahedral, polymeric). In the former, the sulfate acts as monodentate while in the other two as a bidentate bridge between two different Zn centers. There is a variety of sulfate S-O bond lengths, depending on the different coordination conditions and H-bonding interactions.

“Synthesis, structure and magnetic properties of the oxydiacetato-bridged Cu(II)-Ln(III) complexes $[\{ Cu_3Ln_2(oda)_6(H_2O)_6 \} \cdot 12H_2O]_n$ (Ln = Y, Gd, Eu, Nd, Pr)”

R. Baggio, M.T. Garland, O. Peña, M. Perec and E. Spodine

J. Chem. Soc., Dalton Trans., 2000, 13 (2000) 2061

Heterometallic compounds involving the rare earth(III) yttrium, gadolinium, europium, neodymium or praseodymium and copper(II) metal ions with oxydiacetate as the connecting ligand, have been investigated. Five isostructural polymers $[\{ Cu_3Ln_2(oda)_6(H_2O)_6 \} \cdot 12H_2O]_n$ (Ln = Y (1), Gd (2), Eu (3), Nd (4) and Pr (5)) have been obtained and structurally characterized. The Ln atoms in 1 to 5 show tricapped trigonal prism arrangements whereas the Cu atoms show octahedral geometry. The O(ether) atom of the oda ligand is bound exclusively to the Ln centers. Antiferromagnetic exchange interactions dominate in these compounds.

“Catena-poly [[diaqua(phenanthroline-N,N')cadmium(II)- μ -(sulfato-O:O')]] and Catena-poly [[diaqua (2,9-dimethylphenanthroline-N,N')cadmium(II)- μ -(sulfato-O:O')]]”

M. Harvey, S. Baggio, L. Suescun, R. Baggio
Acta Cryst. C56 (2000) 811

Both title compounds $C_{12}H_{12}CdN_2O_6S$ and $C_{14}H_{16}CdN_2O_6S$ are polymeric, and present the

cadmium atoms in very similar octahedral environments, provided by the bidentate organic ligand (phenanthroline/dimethylphenanthroline), two aqua molecules and two oxygens from two translationally related sulfate groups, which thus act as links of the resulting polymeric chains.

“Coordination mode of some polypyridyl ligands towards the platinum(II) complexes $[Pt(dppf)(H_2O)_2](CF_3SO_3)_2$ (dppf = 1,1'-bis(diphenylphosphino)-ferrocene) and $[Pt(Me_2SO)_2Cl_2]$. Crystal structure of the seven-membered chelate ring complex $[Pt(dpq)Cl_2]$ (dpq = 2,3-di(2-pyridyl)-quinoxaline)”

J. Granifo, M.E. Vargas, M.T. Garland, R. Baggio
Inorg.Chim.Acta 305 (2) (2000) 143

Crystals of the title compound are composed of discrete Pt-dpq- C_{12} units, connected through some π - π interactions as well as by hydrogen bonding. The molecular geometry is quite similar to the methylated Pd(II) analog (Cusumano, *Acta Cryst C54, 485-487*, 1998), as are some of the intermolecular interactions present, in spite of the compounds not being isostructural.

“Bis-(2,10-phenanthroline-N,N')-(thiosulfato-O,S)-nickel(II),hydrate, methanol solvate and Bis-(2,2'-bipyridyl-N,N')-(thiosulfato-O,S)-nickel(II),hydrate,methanol solvate”

E. Freire, S. Baggio, R. Mariezcurrena, R. Baggio
Acta Cryst.C56 (2000) 926

The compounds reported, $C_{20}H_{16}N_4NiO_3S_2 \cdot nH_2O \cdot mCH_3OH$ and $C_{24}H_{16}N_4NiO_3S_2 \cdot n'H_2O \cdot m'CH_3OH$ are monomeric, with the nickel(II) ion displaying a distorted octahedral coordination provided by the four nitrogen atoms of two bidentate bipy (phen) groups and one sulfur and one oxygen from a chelate thiosulfate anion. The structures are highly unstable outside their mother liquors, and are stabilized in solution by a not fully determined number of water and methanol solvate molecules. The phenanthroline complex presents two independent moieties related by a non-crystallographic pseudo symmetry center. The thiosulfate anions present the usual S-O lengthening found when the anion acts in a bidentate mode.

**“Aqua-bis(crotonato)-bis-(pyridine)
copper(II)”**

*R. Baggio, B. Foxman, M.T. Garland, M. Perec
and W. Shang*

Acta Cryst. C56 (2000) e505

The title compound, $\text{Cu}(\text{O}_2\text{CCH}=\text{CHCH}_3)_2(\text{py})_2(\text{H}_2\text{O})$, crystallizes as a monomer, with the copper ion in a pentacoordinated square pyramidal environment, bisected by a twofold axis through the cation and the apex. The molecules organize in chains connected by H-bonds running along the unique axis b.

**“X-ray study on the nickel(II)-oxydiacetic
system and its 1,10-phenanthroline and
2,2': 6', 2'' terpyridine adducts”**

R. Baggio, M.T. Garland, M. Perec

Inorg.Chim.Acta, 310 (2000) 81

Three new metal-organic coordination complexes have been prepared and their crystal structures determined: $[\text{Ni}(\text{oda})(\text{H}_2\text{O})_3] \cdot 1.5\text{H}_2\text{O}$, $[\text{Ni}(\text{oda})(\text{phen})(\text{H}_2\text{O})] \cdot 1.5\text{H}_2\text{O}$ and $[\text{Ni}(\text{oda})(\text{terpy})] \cdot 2\text{H}_2\text{O}$ (oda = oxydiacetate, phen = 1,10-phenanthroline, terpy = 2,2': 6', 2'' terpyridine). The oxydiacetate ligand is tridentate in these compounds, being nearly planar in the first two and hinged in the latter. Hydrogen-bonding and p-p interaction is extensive in the three solids.

**“X-ray study of two novel nickel(II)-
thiosulfate compounds”**

E. Freire, S. Baggio, L. Suescun and R. Baggio

Australian Journal of Chem. 532 (9) (2000) 785

Two novel nickel thiosulfate complexes have been prepared and their crystal structures determined: $\text{NiS}_2\text{O}_3(\text{dmph})(\text{H}_2\text{O}) \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ (i) (dmph = 2,9-dimethyl-1,10-phenanthroline), which to our knowledge is the first pentacoordinated nickel thiosulfate complex described so far, and $\text{NiS}_2\text{O}_3(\text{dmph})$ (ii), an hexacoordinated complex which displays a thiosulfate binding mode with no precedents in the literature, viz.: bridging solely through oxygen. Compound (i) is monoclinic, $C2/c$, a 26.269(5), b 7.641(3), c 18.381(3) Å, β 97.00(2)°, V 3662(2) Å³, $Z=8$, conventional R (on F) being 0.049 for 2217 No observed reflexions ($I > 2\sigma(I)$). Compound (ii) is also monoclinic, $P21/n$, a 11.108(2), b 10.955(2), c 11.666(2) Å, β

103.32(3)°, V 1381.4(5) Å³, $z=4$, R 0.036, No 2497.

**“Molecular Structure and Magnetic
Properties of
[Gd(LH₄)(NO₃)₂(H₂O)]NO₃(H₂O)₂,
[Sm(LH₄)(NO₃)₂(H₂O)]NO₃(H₂O)_{1.5}(CH₃OH)_{0.5}
and [Cu₂(LH₂)(H₂O)₂](NO₃)₂ Complexes
(LH₄: Schiff base ligand derived from 4-
methyl-2, 6-diformylphenol and 1,3-
diaminopropanol)”**

*E. Spodine, Y. Moreno, M.T. Garland, O. Pena and
R.F. Baggio*

Inorganica Chimica Acta 309 (2000) 57

Novel lanthanide(III) complexes (Ln = Gd (1), Sm (2), La (3)) of the macrocyclic ligand LH₄ have been prepared and characterized. The binuclear copper(II) complex $(\text{Cu}_2(\text{LH}_2)(\text{H}_2\text{O})(\text{NO}_3)_2)$ (4), has been obtained by transmetalation of complex 3 with $\text{Cu}(\text{CF}_3\text{COO})_2$. The macrocyclic Schiff base ligand (LH₄) is formed by the condensation of two molecules of 4-methyl-2, 6-diformylphenol with two molecules of 1,3-diaminopropanol in the presence of the lanthanide ions. The alcohol group of the macrocycle does not coordinate to the copper(II) centers of the binuclear complex. However, one of the secondary alcohol groups of the ligand coordinates in an asymmetric mode to the lanthanide ion in the corresponding three complexes. The X-ray crystal structures of $(\text{Gd}(\text{LH}_4)(\text{NO}_3)_2(\text{H}_2\text{O}))(\text{NO}_3)(\text{H}_2\text{O})_2$ (1), $(\text{Sm}(\text{LH}_4)(\text{NO}_3)_2(\text{H}_2\text{O}))(\text{NO}_3)(\text{H}_2\text{O})_{1.5}(\text{CH}_3\text{OH})_{0.5}$ (2), and $(\text{Cu}_2(\text{LH}_2)(\text{H}_2\text{O})_2)(\text{NO}_3)_2$ (4) have been determined. Magnetic susceptibility measurements in the 5-300 K range were obtained for these complexes.

**“Iron Oxide Mineralogy of a Mollisol from
Bahía Blanca by Selective Dissolution
Techniques, X-Ray Diffraction and
Mössbauer Spectroscopy”**

*S.G. Acebal, A. Mijovilovich, E.H. Rueda, M.E.
Aguirre and C. Saragovi*

Clays and Clay Min. 48 (3) (2000) 322

Selective dissolution techniques by ammonium oxalate (OX), dithionite-citrate-bicarbonate (DCB), and dithionite-ethylenediaminetetraacetic acid (D-EDTA), X-ray diffraction and Mössbauer

spectroscopy were used to identify and characterize iron oxides and oxyhydroxides in the <2-mm, <50- μm , and <2- μm size fractions of a Mollisol from Bahía Blanca, Argentina. Iron compounds are present at low concentrations in mixtures with quartz, Na-rich feldspar, illite, interstratified illite-montmorillonite, and traces of kaolinite. Total Fe and Al content increases as soil particle-size decreases, from 4.3 and 13.3 wt. % in the <2-mm size fraction to 8.5 and 22.8 wt. % in the clay fraction (<2 μm), respectively. No more than 25-30 % of the total Fe is associated with crystalline and amorphous Fe oxides. Weakly ferromagnetic hematite and goethite were identified in the different fractions. These phases have small particle sizes and/or low crystallinity, and/or Al-substituted sites. Crystalline magnetite or maghemite is scarce. These Fe phases are probably coating coarser particles. In all fractions, the efficiency for Fe removal is highest for the D-EDTA treatment and least efficient for the OX method, regardless of fraction size. The opposite is true for Al removal. Poorly crystallized oxalate-soluble hematite and goethite are only present in coarser fractions. Poorly crystallized and crystalline DCB and D-EDTA-soluble hematite and goethite are present in coarser fractions, but do not exist in the clay fraction. DCB treatment probably dissolves Al in the 2:1 type minerals occurring in this soil, whereas D-EDTA dissolves Fe in hydroxy interlayers or silicate phases.

“Characterization of corrosion layers of low alloy carbon steels in aqueous CO₂ (g) and brine solutions by transmission Mössbauer Spectroscopy”

E. Chung, C. Saragovi, I. Raspini

Corrosion NACE, 56 (8) (2000) 769

Transmission Mössbauer Spectroscopy (TMS), which is a powerful tool for atmospheric and marine corrosion studies, is presented here as a tool for characterising corrosion products formed in aqueous CO_{2(g)} saturated brines. An electrochemical process was applied to simulate a corrosion process at the bottom of an oil well (turbulence and aggressive environment) to obtain corrosion products. Their formation depends on composition of steels and environmental conditions. The characterisation through TMS of corrosion film formed on two low alloy carbon steels, one without Cr and another with 1% Cr, exposed to CO_{2(g)} flushed solutions has shown morphological and qualitative differences between the corrosion films. Ferrous carbonate (FeCO₃, siderite), a faulted cementite (Fe₃C*), and a particular carbide (Fe-C*), both of the latter not reported before, were found in the corrosion products. The so-called Fe₃C* is a cementite with two forms: an alloyed cementite as (Fe,M)₃C (M=Mn, Cr) and/or as Fe_{3-x}C_{1+x}, a cementite with more carbon atoms as interstitials. The Fe-C* carbide is possibly a small particle Fe-C phase with also two possible forms. Fe₃C* and little of Fe-C* carbides were identified on the probes without chromium. FeCO₃ and Fe-C carbide were identified on the probes with 1% Cr, being FeCO₃ the more adhesive constituent firmly linked to the base metal. It is suggested that the alloying elements in the steel (Cr in this case) other than Fe²⁺ ion concentration and neutralising agents are responsible for the formation of FeCO₃. The better performance of the 1% Cr containing steel can be related to the presence of a protecting film formed by a mixture of both Fe-C* carbide and FeCO₃.