Coordination Chemistry Reviews
172 (1998) 157–180

Chromium 1996

David K. Geiger *

Department of Chemistry, SUNY-College at Geneseo, 1 College Circle, Geneseo, NY 14454-1507, USA

Contents

1. Introduction

This review covers the coordination chemistry of chromium published in 1996. Although not comprehensive, this review aims to provide a broad and representative survey of the literature of the period. Volumes 124–126 of Chemical Abstracts, CARL UnCover Online, and the indices of major journals in the area were used to obtain the citations included herein. In general, organometallic complexes are not covered. The organization used is similar to that employed in previous years with particular emphasis placed on the ligand systems.

2. Chromium(VI)

The crystal structures of the salts of a series of organic bases were determined [1]. The salts 4,4′-bipyridinium bis[chlorochromate(VI)], 4-methylquinolinium

---

* Corresponding author. E-mail: geiger@geneseo.edu

PII S0010-8545(98)00108-8

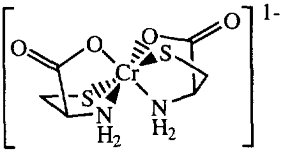
chlorochromate(VI), 6-methylquinolinium chlorochromate(VI), *N,N'*-ethylenediaminium chloride chlorochromate(VI), and (5-chloro-2-pyridyl)(2-pyridyl)-ammonium chlorochromate(VI) display average Cr–O bond distances between 1.588(4) and 1.622(2) Å. The observed Cr–Cl distances range from 2.158(1) to 2.189(1) Å. The angles about the Cr are in the range 106.2(1) to 113.7°. N–H···O hydrogen bonding is observed with N···O distances from 2.760(3) to 3.209(5) Å and N–H···O angles from 119.2(2) to 161.1(4)°.

The nitrido complex $Cr(N)(O^tBu)_3$ was characterized by X-ray diffraction [2]. The complex is monomeric in the solid state and exhibits C_{3v} symmetry. The Cr–N distance is 1.538(5) Å and the average Cr–O distance is 1.74 Å. The average N–Cr–O and O–Cr–O angles are 108.2 and 111.0°, respectively.

Ab initio procedures and density functional theory (DFT) were used to examine the geometrical, vibrational and electronic structures of the series of complexes CrO_2X_2 (X = F, Cl, Br, I) [3]. It was found that DFT methods gave a more accurate geometry than HF and post-HF methods for CrO_2F_2. Bond distances and angles are reported for the Br and I analogues, for which experimentally determined structural data are not available. The HOMO–LUMO transitions decrease from F to I, which is as expected based on the electrochemical series. The results confirm the relative instability of the Br and I analogues. The authors conclude that the failure of VSEPR theory to predict the structure for CrO_2F_2 results from the large degree of ionic character in the Cr–F bond, leading to coulombic repulsion between the fluoride ligands.

The reaction of potassium dichromate with γ-glutamylcysteine, *N*-acetylcysteine, and cysteine results in the formation of 1:1 Cr(VI) complexes with cysteinyl thiolate ligands [4]. Multinuclear NMR spectroscopic studies showed that the coordination mode is monodentate, forming complexes of the type $RS\text{-}CrO_3^-$. EPR spectroscopy was used to show that formation of Cr(V) via a one-electron process is only a minor reaction pathway.

Using kinetic data obtained for the reduction of CrO_4^{2-} to Cr(III) by cysteine in neutral aqueous solution, a mechanism was proposed [5]. The main product of the reduction was determined to be *N*(*cis*),*O*(*cis*),*S*(*trans*)-bis(L-cysteinato)-chromate(III) (**1**) from UV–vis and CD spectroscopies. The proposed mechanism involves a sequential three-electron reduction, leading to the penultimate product *N*,*O*,*S*(L-cysteinato)-*N*,*S*(L-cysteinato)(hydroxo)chromate(III), which undergoes an intramolecular lactonization at the metal center to give the final product.

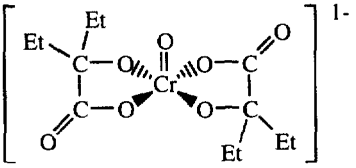


(**1**)

3. Chromium(V)

The synthesis and structure of [Cr(N)(tacn)(acac)]ClO_4 was reported [6]. The complex was prepared by photolyzing a solid sample of [Cr(N_3)(tacn)(acac)]ClO_4. The corresponding phen, pic, and 2,2,6,6-tetramethylheptane-3,5-dionate complexes were prepared in a like fashion. Photolysis of solid Cr(N_3)(tacn)(ox) resulted in the formation of a mixed oxidation state dinuclear species (see Section 7). However, Cr(N)(tacn)(ox) was prepared by photolyzing a dmso solution of Cr(N_3)(tacn)(acac). The structure of [Cr(N)(tacn)(acac)]ClO_4 exhibits distorted octahedral geometry with a *fac* tacn ligand arrangement. A mirror plane bisects the ox and tacn ligands. The Cr–N(nitride) distance is 1.575(9) Å. The Cr–N(amine) distance *trans* to the nitride ligand is substantially longer than the symmetry equivalent *cis* Cr–N(amine) distances, 2.350(11) Å and 2.069(9) Å, respectively. The (nitride)N–Cr–N(amine) angles are 96.4(3)° and 170.5(4)°. The (amine)N–Cr–N(amine) angle is 76.6(3) Å. The symmetry independent Cr–O distance is 1.938(6) Å.

The oxidation of DNA model substrates 5,5-dimethylpyrroline *N*-oxide (DMPO) and phenyl-*N*-tert-butylnitrone (PBN) by the complex anion [Cr(ehba)$_2$O]$^-$ (**2**) was examined [7]. The reactions were found to be pH dependent and involve a radical and a nonradical pathway. The nonradical pathway dominates at lower pH, but the radical pathway is observed at physiological pH.

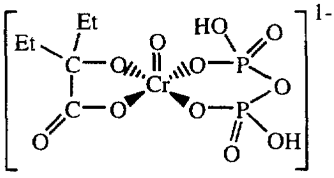


(2)

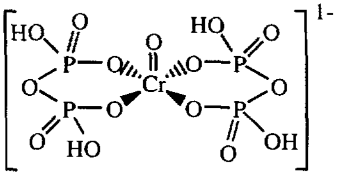
In a second study, the reactions of (**2**) with pyrophosphate and with free phosphate were carried out as models of didentate and monodentate phosphate linkages between Cr(V) and deoxyribonucleotides [8]. Two Cr(V)-pyrophosphate species, (**3**) and (**4**), were observed by EPR upon reaction with pyrophosphate. Reaction with free phosphate resulted in the formation of the *fac* and *mer* isomers (**5**) and (**6**). The significance of these observations with respect to oxidation of DNA by Cr(V) was dizscussed.

Complex (**2**) was shown to exhibit a pH dependent Cr(V/IV) redox couple at 0.44 V vs. NHE [9]. At pH 3.5 to 5, the couple is quasi-reversible. At pH 3.5 to 2.5, the couple is shifted to 0.64 V vs. NHE. At pH<2.1, only a two-electron reduction wave corresponding to Cr(V/III) is observed. Using a potentiometric titration of (**2**) with hexacyanoferrate(II), the Cr(V/III) potential was determined to be 0.85 V vs. NHE. Evidence to support the argument that Cr(IV) complexes exist in an equilibrium between mono and bis ehba^{2-} coordination was presented.

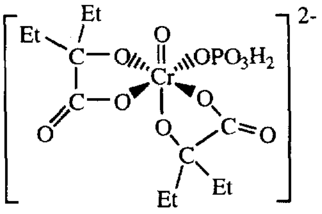
The reduction of the Cr(III) complex $(H_2O)_2$(cyclam)$CrOO^{2+}$ by Cr^{2+} was examined [10]. The overall stoichiometry is as shown in Eq. (1). The reaction



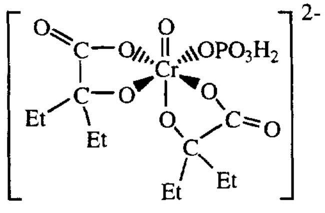
(3)



(4)



(5)



(6)

involves the initial one-electron process to yield $(H_2O)_2(cyclam)CrOOH^{2+}$. Further reduction by Cr^{2+} yields the observed product. The initial one-electron step was supported by reacting the peroxo complex with a stoichiometric amount of Fe^{2+} followed by titrating the resulting Fe^{3+} with Cr^{2+}. The hydroperoxide complex decomposes to form an intermediate Cr(V) complex. Based on the axial symmetry of the ESR spectrum and the *g* values obtained, the formula of the intermediate was assigned $(cyclam)CrO^{3+}$. The Cr(V) complex decomposes via an intramolecular redox process to yield a Cr(III) complex with an oxidized cyclam ligand.

$$(H_2O)_2(cyclam)CrOO^{2+} + 3Cr^{2+} + 4H^+ \rightarrow (cyclam)Cr(H_2O)_2^{3+} + 3Cr^{3+} + H_2O \tag{1}$$

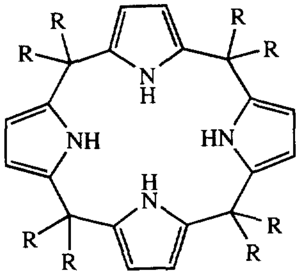
The reaction of $[CrCp_2^*Br_2]_2$ with two equivalents of $Li(^tBuNSPh)$ resulted in the isolation of $CrCp^*(N^tBu)(SPh)^2$ [11]. The authors suggest that the product results from the N–S bond cleavage from an intermediate sulfenamido complex. The complex exhibits a tetrahedral geometry with the Cp^* ring occupying one of the sites, two sites occupied by benzenethiolate ligands and the final site by the tert-butylamide. The Cp^* ring is coordinated in a symmetrical fashion with the Cr–C distances in the range 2.244(5) to 2.286(5) Å. The Cr–S distances are 2.301(2) and 2.327(2) Å. The Cr–N distance is 1.620(3) Å. The complex is a paramagnetic d^1 species and exhibits a temperature dependent ESR spectrum.

4. Chromium(IV)

The oxochromium porphyrin complexes Cr(IV)(tpp)(O)(pyR), where pyR is py, 2-methylpyridine, or 3,5-dimethylpyridine, were prepared by the chemical reduction of Cr(tpp)Cl in the presence of the pyridine ligand followed by air oxidation [12].

The complexes were characterized by NMR, ESR, UV–vis and IR spectroscopy. Reaction of the complexes with cyclohexene or styrene produced 2-cyclohexene-1-ol or styrene oxide, respectively.

The two-electron oxidation of $[Cr(orpg)Li_2(thf)_4]$ by N_2O or O_2 results in the formation of the Cr(IV) complex $[(thf)(orpg)Cr(O)(thfLi)_2]$, where $orpgH_4$ is octaalkylporphyrinogen (7) with R = Et or ^{n}Pr [13]. The complex has a (thf)O–Cr–O(oxo) angle of 177.4(3)° and average N–Cr–N angles of 89.35° and 177.2°. The Cr–O(oxo) and Cr–O(thf) distances are 1.990(6) Å and 2.082(6) Å, respectively. The average Cr–N distance is 2.05 Å. The Li cations are coordinated to adjacent pyrrole rings on the same side of the macrocycle in η^5 fashion. They are each coordinated to the oxo ligand and to different thf ligands. The Li–O–Li group has an angle of 135.2(8)° and the Li–O(oxo) distances are 1.88(2) and 1.89(2) Å.



(7)

5. Chromium(III)

5.1. Complexes with monodentate ligands

$Cr[N(SiMe_3)_2]_3$ was synthesized in high yield from $(Me_3tac)CrCl_3$, where Me_3tac is the tridentate ligand *N,N′,N″*-trimethyl-1,3,5-triazacyclohexane [14]. The complex was crystallized as the hemi-hexamethyldisiloxane derivative and the structure obtained. The Cr atom sits on a three-fold axis in the plane of the three nitrogen atoms. The Cr–N distance is 1.889(2) Å. The solvent is slightly disordered and located in the large channels formed by the chromium complex.

The crystal structure of *trans*-$[CrCl_2(NH_2R)_4]Cl$, where R = Et, was determined and kinetic studies of the Hg^{2+} assisted chloride release of the complexes with R = Et, Pr, Bu were performed [15]. The symmetry independent Cr–Cl distance is 2.323(1) Å and Cr–N distances are 2.092(2) Å and 2.098(2) Å. The Cl–Cr–Cl angle is 179.998(1)°. The alkyl arms of the coordinated $EtNH_2$ groups adopt the +,+,−,− conformation. The displacement of the chlorides occurs in two discreet steps. The data suggest that the incoming water trajectory is the same for both steps with the water molecule approaching the octahedral face comprised of two nitrogens and adjacent to the Cr–Cl–Hg bridge formed in a fast encounter process.

$Cr(NH_3)_5(py)^{3+}$ was isolated as the perchlorate salt from $Cr(NH_3)_5(dmso)^{3+}$ in pyridine [16]. In aqueous solution, two LF bands are observed at 467 and 352 nm. A pyridine localized LL band is observed at 260 nm. The complex is luminescent at room temperature. The 668 nm band was assigned to $^2E_g \rightarrow {}^4A_{2g}$ phosphorescence. Irradiation of the LF or LL bands results in loss of either the py or an ammonia ligand to comparable extents, with the quantum yield for py loss slightly greater. Thermal aquation rates indicate that py aquation is about three times faster than NH_3 aquation.

The crystal structures of $[Cr(NH_3)_5(NH_2{}^tBu)](ClO_4)_3 \cdot 2H_2O$ and $[Cr(NH_3)_5(NH_2{}^tBu)]ZnCl_4Cl \cdot H_2O$ were reported [17]. The perchlorate complex was prepared by reacting $[Cr(NH_3)_5(O_3SCF_3)](CF_3SO_3)_2$ in neat $NH_2{}^tBu$ and precipitating the crude product from aqueous solution via addition of $HClO_4$. The corresponding complexes with the ^tBu group replaced by Me and ^nPr were prepared in analogous fashion using the appropriate amine. The ^tBu complex is stable in aqueous solution for several hours. The stability is presumably the result of the steric bulk of the ligand shielding the metal against incoming ligands. The structure of the tetrachlorozincate salt exhibits an average $Cr–NH_3$ distance of 2.086 Å and a substantially elongated $Cr–NH_2{}^tBu$ distance of 2.132 Å. The perchlorate salt has an average $Cr–NH_3$ distance of 2.063 Å and a $Cr–NH_2{}^tBu$ distance of 2.113 Å.

The syntheses of $[Cr(NH_3)_5(PhPO_3H)](ClO_4)_2$ and $[Cr(NH_3)_5(PhHPO_2)](ClO_4)_2$ from $[Cr(NH_3)_5(H_2O)](ClO_4)_3$ and phenylphosphonic acid and phenylphosphinic acid, respectively, were reported [18]. An AOM analysis was performed. The authors conclude that the ligand field of the ammines is decreased more for the oxyphosphorus complexes than for carboxylate complexes.

Reaction of *fac*-$[Cr(NH_3)_3(O_3SCF_3)_3]$ with LiX, X = Cl or Br, in thf resulted in the formation of *fac*-$[Cr(NH_3)_3(X)_3]$ [19]. UV–vis spectral properties were reported. The complexes are monomeric and exhibit spectra and magnetic properties expected for a d^3 system.

An EXAFS study was reported for the series of complexes $[CrCl_n(H_2O)_{6-n}]^{(3-n)+}$, where $n = 1–3$ [20]. The average Cr–O and Cr–Cl distances are 2.00 and 2.30 Å, respectively. Ordering beyond the first coordination sphere between 3.9 and 4.5 Å was observed for each species. The second sphere is composed only of water for $n = 0$ or 1. For $n = 2$, there is a contraction of Cr–O to 3.88–3.89 Å, a decrease in coordination number for this second hydration shell, and outer-sphere chloride ligands appear at 4.4 Å. For $n = 3$, the second coordination sphere is composed of seven chloride anions at 4.3 Å.

Variable temperature ^{17}O NMR spectroscopic measurements and molecular modeling experiments were used to examine the second coordination sphere water exchange rate for hexaaquachromium(III) [21]. For molecular dynamics simulations, the geometry of the cation was constrained to T_h symmetry. The authors conclude that a well-defined second coordination shell exists in aqueous solution with a coordination number of 12.94. The water dipoles point toward the ion with a first sphere hydrogen to second sphere oxygen distance of only 1.42 Å. The lifetime of the water in the second coordination sphere of the chromium ion is 128 or 144 ps as determined by NMR spectroscopy and molecular dynamics simulations, respectively.

Mechanistic studies of the anation of $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5(OH)]^{2+}$ by L-histidine were reported [22]. The anation proceeds by an outer-sphere process for each reactant. The hexaaquachromium ion reacts via an I_a mechanism, whereas the hydroxo species reacts via an I_d mechanism. The assignments are supported by comparing isotopic water-exchange rate constants for the two cations and by results of experiments carried out with solvent systems having varying dielectric constants.

The mechanism of formation of amino acid–Cr(III)–DNA complexes in vitro and base specificity of the adduct formation were examined [23]. When DNA-bound Cr(III) was reacted with histidine or cysteine, no complexation of the amino acids occurred. Reaction of preformed Cr(III) histidine or cysteine complexes with DNA resulted in the formation of ternary DNA adducts. Further studies showed that Cr(III)–histidine reacts to form ternary complexes with deoxynucleotides but not deoxynucleosides. Because the histidine adduct reacts with all deoxynucleotides, the authors conclude that there is little or no involvement of the base group in the ternary complex formation. No base preference was observed with Cr(III)–cysteine adducts. The results suggest that the phosphate groups are the primary binding sites on DNA for Cr(III)–amino acid complexes.

The complex $[Cr(OH_2)_6][Na][tscs]\cdot(acetone)\cdot 10.5H_2O$ was prepared from the sodium salt of calix[4]arenesulphonate, $tscs^{4-}$, and $Cr(NO_3)_3$ [24]. The complex was characterized by IR and UV–vis spectroscopy. A magnetic moment of 4.96 μ_B was determined. All data are consistent with a lack of coordinate of either the phenolic or sulfonic acid residues of the $tscs^{4-}$. Rather, the calixarene is in the second coordination sphere with H-bonding between the sulfonic acid residues and three-coordinated water ligands sharing a triangular face of the Cr(III) coordination sphere.

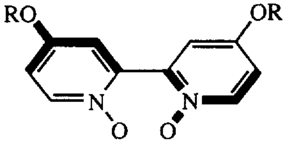
5.2. Complexes with didentate ligands

5.2.1. Oxygen donor ligand systems

The complexes $[Cr(bpdoOR)_3]^{3+}$, where bpdoOR is 2,2′-bipyridine-1,1′-dioxide (**8**) and R = Me or Et, were reported [25]. The complexes form two diastereomeric pairs, Δ(λλλ) and Λ(δδδ); Δ(λλδ) and Λ(δδλ), which were separated and resolved by column chromatography. The isomers isomerized and racemized in water. The rate of isomerization showed first order kinetics. The equilibrium constants for both complexes are close to one. Activation parameters were also reported.

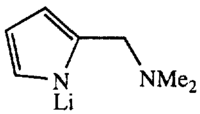
5.2.2. Nitrogen donor ligand systems

Reaction of $CrBr_3\cdot 3thf$ and lithium 2-(dimethylaminomethyl)pyrrolide, LiDMAMP (**9**), resulted in the isolation of the complex *fac*-$[Cr(DMAMP)_3]$ [26].



(8)

The complex exhibits a magnetic moment of 3.86 μ_B. The complex exhibits a trigonally distorted octahedral geometry with average Cr–N(pyrrolide) and Cr–N(amine) distances of 1.968(15) Å and 2.290(14) Å. The average N(amine)–Cr–N(pyrrolide) angle is 77.9(1)°. The chelate ring is decidedly nonplanar with the amine nitrogen atom about 0.7 Å out of the plane formed by the other four atoms.



(9)

An examination of the Zeeman splittings of spin-forbidden transitions of $[Cr(bpy)_3]^+$ complexes was presented [27]. The splittings are consistent with AOM calculations and σ and π interactions were considered. The splittings result from trigonal distortions and phase-coupling between the dπ and bpy π orbitals. The larger splitting observed for the ClO_4^- salt compared to the PF_6^- salt was found to result from the greater distortion in the ClO_4^- salt. A comparison between bpy and acac was also made.

Using high-pressure cyclic volumetric techniques, the redox reaction volume of $Cr(bpy)_3^{3+}$ was examined [28]. The formal potential for $Cr(bpy)^{3+/2+}$ was found to be −0.8951 V vs. $Ag/AgNO_3$ at 0.1 MPa. The reaction volume determined was only +8.1 $cm^3\ mol^{-1}$, consistent with the small change in Cr–N distance accompanying the change in oxidation state. The results are discussed with respect to the larger values found for Co complexes.

The syntheses of the complexes $[Cr(N_3)(bpy)(H_2O)_3]^{2+}$ and $[Cr(bpy)(H_2O)_4]^{3+}$ were reported [29]. $[Cr(bpy)(H_2O)_4]^{3+}$ was synthesized from $[Cr(bpy)(C_2O_4)_2]^-$ by Fe^{3+} induced aquation. The reaction mixture was purified via column chromatography and the complex ion was isolated as the perchlorate salt. Anation of $[Cr(bpy)(H_2O)_4]^{3+}$ by HN_3 resulted in the formation of $[Cr(N_3)(bpy)(H_2O)_3]^{2+}$, which was isolated as the perchlorate salt. Resolution of the two geometrical isomers was not accomplished. A Cr^{2+} catalyzed aquation study of $[Cr(N_3)(bpy)(H_2O)_3]^{2+}$ was performed. The products included $[Cr(N_3)(H_2O)_5]^{2+}$ (80%) and $Cr^{3+}(aq)$ (20%). In the absence of Cr^{2+}, only slow azide substitution occurs. Kinetic data support the formation of an inner-sphere electron transfer process.

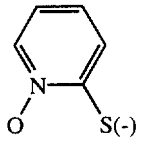
5.2.3. Mixed donor ligand systems

The racemization kinetics between the Λ and Δ forms of the amino acid complex *fac*-[Cr(val)$_3$] were studied in dmf [30]. The complexes undergo conversion to complexes of the type [Cr(val)$_2$(val-N)(dmf)], where val-N represents monodentate, N-bound val, followed by a twist about the former C_3 axis leading to racemization. Rate constants and activation parameters for the square-network reaction system were reported.

CD and FAB-MS techniques were used to examine a series of Cr(III) (aa)$_3$ complexes, where aaH represents the amino acids valH, leuH, and isoleuH [31]. Only the ala complex was shown to be a single compound with a *tris*-chelate structure. The results suggest that the other samples were mixtures of *tris*, *bis*, and dimeric compounds. The authors conclude that FAB-MS has potential for use as a technique for studying the nature of this type of compound and Cr(III) species in general.

The complexes Cr(cys)$_3$, Cr(cyt)$_3$, Cr(dtnb)(cys)$_2$, CrCl$_3$(dbs)$_3$, and (NH$_4$)$_3$[CrCl$_3$(msa)$_3$], where cysH is cysteine, cytH is cystine, dtnbH is dithiobisnitrobenzoic acid, dbs is dibenzydisulfide, and msaH is α-mercaptosuccinic acid, were reported [32]. The complexes were synthesized from CrCl$_3$py$_3$ and an equimolar amount or a three-fold excess of ligand. The products were characterized by IR, UV–vis, and CD spectroscopy. The magnetic moments are close to the predicted spin-only value for Cr(III). Cyclic voltammetric data are also reported. The data are consistent with no coordination of sulfur for the cys, cyt, and msa complexes. However, the dbs and dtnb complexes do exhibit sulfur coordination.

The crystal structure of Cr(mpo)$_3$ was reported, where mpo$^-$ is the didentate ligand which is the conjugate base of 2-mercaptopyridine N-oxide (**10**) [33]. The complex was isolated as the acetone solvate. The complex possesses a *fac* geometry with average Cr–S and Cr–O distances of 2.363(1) Å and 1.986(2) Å, respectively. The average ligand bite angle is 83.3(1)°. The average angle formed by *trans* ligands is 170.2°.



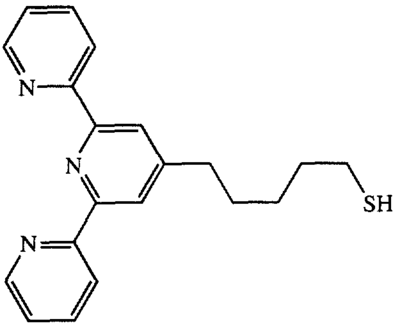
(10)

5.3. Polydentate ligands

[Cr(HBpz$_3$)$_3$)$_2$]ClO$_4$ was prepared and characterized [34]. The optical and NMR spectroscopies were examined to determine ligand field parameters, which were compared to hexam(m)ine complexes. The AOM was used to describe the absorption characteristics of the complex. The large energy separation between lower energy doublet states and splitting between the first and second quartet bands is caused by anisotropy in the metal–pyrazolyl π bonding.

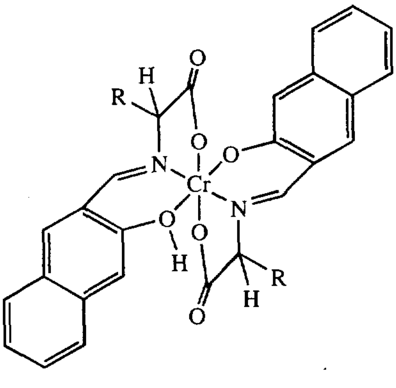
The synthesis of [(tren)Cr(OH)(OH$_2$)]ClO$_4$ was reported [35]. The complex was formed by gentle heating of an aqueous solution of [(tren)CrCl$_2$]Cl with NaOH, followed by treatment with perchloric acid. Excessive heating results in the formation of dinuclear species (see Section 7). The complex was used as the precursor to hydroxo and acetato bridged species.

Gold electrodes were modified with a layer of [Cr(tpy-SH)]$^{3+}$, where tpy-SH is the mercaptopentyl derivative of tpy (**11**) [36]. Under a nitrogen atmosphere, the immobilized complex exhibits a reversible reduction wave at −0.29 V vs. Ag/AgCl. With NO present, a dramatic increase in the cathodic current occurs, suggesting the electrocatalytic reduction of NO.



(11)

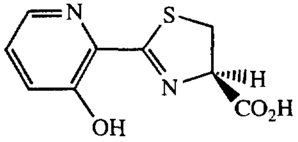
The complexes [Cr(npaa)$_2$] (**12**) were reported [37]. The structural assignment was based on data from elemental analyses, electronic and infrared spectroscopy, and molar conductance studies.



R
H
CH$_3$
CH$_2$CH$_2$CH$_3$
CH$_2$OH
CH$_2$CH(CH$_3$)$_2$
CH(CH$_3$)CH$_2$CH$_3$

(12)

Reaction of $CrCl_3 \cdot 3thf$ with nordesferriferrithiocin, $ndfftH_2$ (**13**), in the presence of triethylamine results in the formation of a solid mixture of isomers of $Et_3NH[Cr(ndfft)_2] \cdot (CH_3)_2CO$ [38]. The ligand coordinates in a tridentate fashion employing the phenolic oxygen, a carboxyl oxygen, and the imine of the five-membered ring. Five possible isomers exist, two meridional and three facial. The two meridional isomers are diastereomers. Three fractions were collected upon performing HPLC. Characterization of the fractions by UV–vis spectroscopy, CD, and FAB-MS allowed the authors to conclude that two of the fractions were A isomers and that the other was a C isomer.



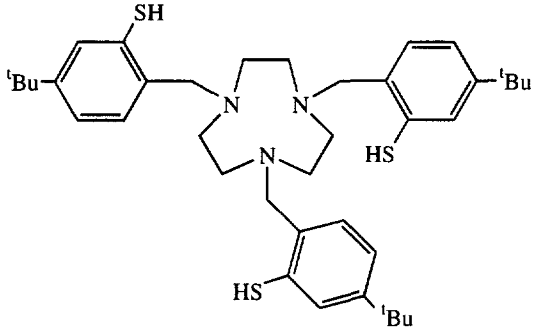
(13)

The reduction of Cr(VI) with the thiols cysH, cysteine ethyl ester (cysOEtH), and mercaptopropanediol ($mpdH_2$) was used to prepare a number of Cr(III) complexes [39]. Reaction of K_2CrO_4 with cysH resulted in the formation of $K[Cr(cys)_2] \cdot 2H_2O$ and $K_2[Cr(O)(cys)(cytH)] \cdot 2H_2O$, where $cytH_2$ is cystine. Reaction with cysOEtH results in the formation of a dinuclear complex (see Section 7). Reaction with $mpdH_2$ gave a product with the formula $K[Cr(mpd)(mpd\text{-}ox)] \cdot 2H_2O$, where mpd-ox represents the oxidized ligand. The complexes were characterized by IR, NMR, and UV–vis spectroscopy. Voltammetry and magnetic susceptibility experiments were also performed. The results of studies involving the interaction of the complexes with DNA were discussed.

The acid dissociation constants for the complex *fac*-$[Cr(tacn)(H_2O)_3]^{3+}$ were obtained [40]. The successive pK_as are 4.538(8), 6.784(8), and 8.883(10). Thermodynamic parameters were also reported. ΔH° is essentially constant for the successive processes, whereas ΔS° displays a significant decrease from positive to negative values and, hence, is responsible for the decrease in the consecutive K_a values. When compared to analogous complexes of other metals, the order of decreasing acidity is Cr(III) > Co(III) > Ir(III) > Rh(III).

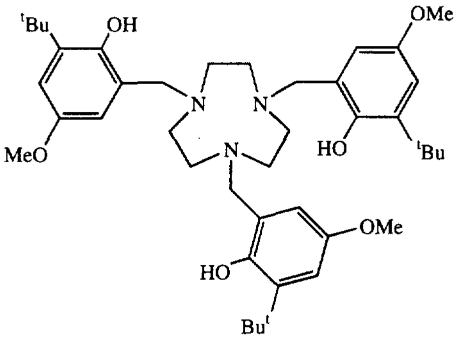
The synthesis of the complex $Cr(L)_3$, where L is (**14**), was accomplished by reacting LH_3 with $Cr_2(acetate)_4 \cdot 4H_2O$ in the presence of base [41]. The absorption spectrum displays d–d transitions at 460 and 591 nm. The Dq and B values of 1690 and 445 cm^{-1}, respectively, indicate considerable covalency of the Cr–S bonds. Intense thiophenolate-to-metal charge-transfer bands were observed at 357 and 410 nm. The complex displays one irreversible oxidation process at 0.65 V vs. Ag/AgCl and two other oxidation steps above 1.00 V. An irreversible reduction step is observed at about −0.6 V vs. Ag/AgCl.

The complexes Cr(L′) and Cr(L″), where $L'H_3$ is (**15**) and $L''H_3$ is (**16**), were reported [42]. Cyclic voltammetric analysis of the complexes reveals three successive

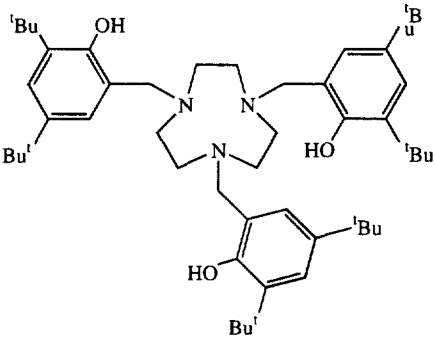


(14)

one-electron, reversible, ligand-centered oxidations. Chemical oxidation of the complexes allowed the isolation of the one-electron oxidized products, $[Cr(L')]ClO_4$ and $[Cr(L'')]ClO_4$. Crystal structures of Cr(L′) and $[Cr(L')]ClO_4$ were determined. The neutral complex exhibits C_3 symmetry with three-coordinated phenoxide ligands. The Cr–O and Cr–N bond distances are 1.920(3) and 2.100(4) Å, respectively. In the monocation, two-coordinated phenoxide ligands have an average Cr–O distance of 1.920 Å. A coordinated phenoxyl radical has a Cr–O distance of 1.943 Å. Magnetic susceptibility data show that Cr(L′) and Cr(L″) have temperature independent magnetic moments of 3.87 μ_B. However, $[Cr(L')]ClO_4$ and $[Cr(L'')]ClO_4$ have temperature independent magnetic moments of 2.83 μ_B, resulting from strong intramolecular antiferromagnetic interactions between the Cr(III) and the phenoxyl radical. These results are supported by EPR data, suggesting that the electrogenerated $[Cr(L'')]^+$, $[Cr(L'')]^{2+}$ and $[Cr(L'')]^{3+}$ have $S=1$, 1/2, and 0 ground states, respectively.

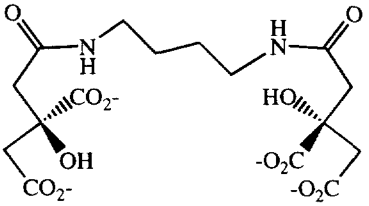


(15)



(16)

The synthesis and spectroscopic data were reported for the two Cr(III) complexes formed by reaction of rhizoferrin (**17**) with $CrCl_3 \cdot 3thf$ in dmso [43]. The two products were separated using chromatography. The relative amounts of the two products formed were dependent on the strength of the base employed in the synthesis, with a stronger base giving the more polar complex. The two complexes could not be interconverted by changing the pH. However, the CD and optical spectra of each species were pH dependent. Mass spectral data suggest that the complexes are geometrical isomers. CD spectra were used to conjecture that both isomers have a *trans* geometry. EPR spectra of both exhibit axial symmetry.



(17)

An examination of the acid ionization of the protonated pendant arm in Cr(edtaH)(H_2O) revealed an unusual positive molar volume change ($+5.1 \pm 0.6$ cm^3 mol^{-1}) [44]. The authors suggest that this results because the complex enters into an equilibrium in which the quinquedentate ligand becomes sexidentate with concomitant expulsion of the water ligand. An analysis of the NCS^- substitution on Cr(edtaH)(H_2O) and $[Cr(edta)(H_2O)]^-$ supports a transient chelation mechanism for substitution in Cr(III) edta complexes.

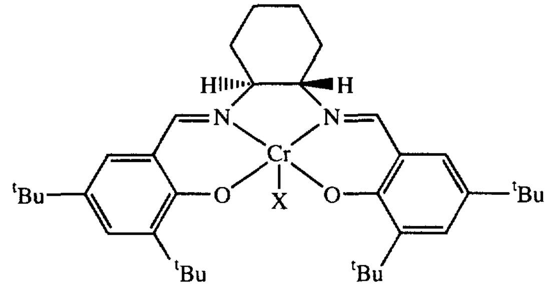
5.4. Macrocyclic ligands

Reaction of $[Cr(H_2O)_2(pc)]I_x$ with $(PPN)NO_2$ resulted in the isolation of the PPN^+ salt of $[Cr(pc)(NO_2)]^-$ [45]. The nitrite ligands are monodentate O-coordinated. The Cr atom sits on a crystallographically imposed inversion center. The average Cr–O and Cr–N distances are 1.9898(14) and 1.981(2) Å, respectively. The Pc^{2-} exhibits a saddled geometry with the β-benzpyrrole atoms ranging from 0.07 Å above to −0.08 Å below the mean plane of the macrocycle. Spectroscopic data including UV–vis, IR and RR are reported.

The crystal structure of $[Cr(cyclam)(OH)(H_2O)]Br_2 \cdot H_2O$ was reported [46]. Each of the axial O atoms possesses a clearly defined H atom and a second H atom that has an occupancy of 50%. The Cr and N atoms are planar within 0.0091 Å. The average Cr–O and Cr–N distances are 1.982(8) Å and 2.064(4) Å, respectively.

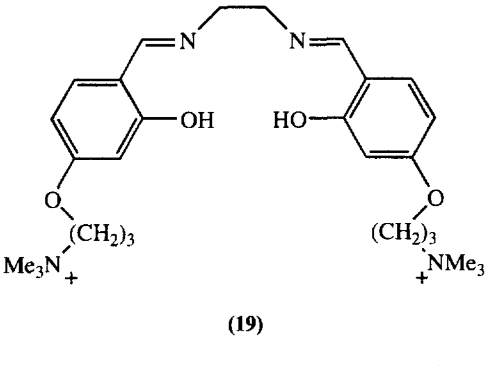
$[Cr(orpg)(thf)_2][Li(thf)_4]$, where $orpgH_4$ is octaalkylporphyrinogen (7), with R = Et or Pr, was prepared from $CrCl_3 \cdot 3thf$ and $orpg[Li(thf)]_4$ [47]. The salt was also prepared by exposing $[Cr(orpg)Li_2(thf)_4]$ to N_2O. A crystal structure of the methyl analogue was obtained. The $[Cr(orpg)(thf)_2]^-$ ion displays average Cr–N and Cr–O distances of 2.046(7) and 2.040(11) Å, respectively. The O–Cr–O angle is 178.8(2)°. The porphyrinogen ligand adopts a saddle-shaped conformation.

The mechanism of (salen)Cr(III) catalyzed asymmetric epoxide ring opening by trimethylsilyl azide, $TMSN_3$, was investigated [48]. The system examined used the salen derivative, salenR, catalyst represented by (**18**). The studies suggest that the complex with $X = Cl^-$ is converted to $X = N_3^-$ before the catalytic process and that the $[Cr(salenR)(N_3)]$ complex is the actual catalyst. The authors suggest that a polymeric system with bridging azides is disrupted by coordination at the second axial site of (**18**). This suggestion is supported by solubility data and the isolation and crystal structure of $[Cr(salenR)(N_3)(thf)]$. Reaction of $[Cr(salenR)(N_3)]$ with cyclopentene oxide in the absence of trimethylsilyl azide resulted in the stoichiometric transfer of the azide and a new complex with an O-coordinated 1-azido-2-cyclopentanoxide. The crystal structure of this complex revealed a monomeric salenR complex with thf and the azidoalkoxide in the axial sites. A catalytic cycle for the catalyzed ring-opening of epoxides by $TMSN_3$ was proposed.



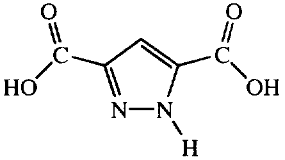
(18)

The new water soluble, dicationic salen derivative (**19**) was reported [49]. The Cr(III) complex was prepared by treatment with $Cr(OAc)_3$. Contrary to findings with the Mn(III) derivative, the Cr(III) exhibits no DNA nicking ability.



(19)

Two complexes with the formulas $Na_2[Cr(eddp)(pzdc)] \cdot 6H_2O$ and $Na_2[Cr(eddp)(pzdc)] \cdot 4.5H_2O$, where pyrazole-3,5-dicarboxylate is $pzdcH_3$ (**20**) and $eddpH_2$ is ethylenediamine-*N*,*N'*-dipropionate, were characterized [50]. Whereas $pzdc^{3-}$ is often a bridging ligand (see Section 7), ^2H NMR spectra provide strong evidence that these complexes are mononuclear. The complexes are likely geometrical isomers of unsym-*cis* corresponding to *mer*- and *fac*-[Cr(eddp)(pzdc)]$^{2-}$. Failure to form dinuclear complexes may be due to the close nonbonded contact that would result.



(20)

The syntheses of the complexes [Cr(N_3)(tacn)(ox)], [Cr(N_3)(tacn)(phen)](ClO_4)$_2$, and [Cr(N_3)(tacn)(LL)]ClO_4, LL = acac, pic, and 2,2,6,6-tetramethylheptane-3,5-dionate, were reported [51]. The complexes exhibit magnetic moments in the range 3.6–3.9 μ_B. Photolysis of all but the ox^{2-} complex results in the loss of N_2 yielding mononuclear Cr(V) nitrido species. Photolysis of the ox^{2-} complex gives a mixed-valent, μ-nitrido-bridge Cr^{III}Cr^{V} complex (see Section 7). The complexes exhibit strong $\nu(N_3^-)$ asymmetric stretching bands in the range 2050–2084 cm^{-1}.

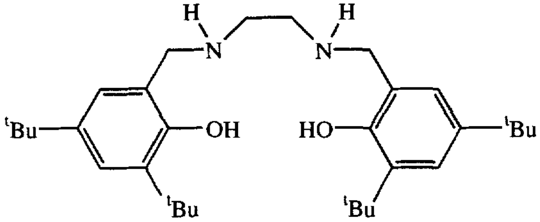
6. Chromium(II) complexes

The synthesis of the silated phosphanimine $CrCl_2(Me_3SiNPMe_3)_2$ was reported [52]. The complex was obtained by reacting $CrCl_2 \cdot 2thf$ with $Me_3SiNPMe_3$ in refluxing CH_2Cl_2. The complex exhibits a Cr–Cl stretching frequency of 401 cm^{-1}. The crystal structure was determined. The square planar complex is in the *trans* configuration with the Cr atom sitting on a center of symmetry. The Cr–N and Cr–Cl distances are 2.117(2) and 2.3594(9) Å, respectively. The N–Cr–Cl angle is 90.45(8)°.

[Cr(orpg)Li_2(thf)$_4$], where orpgH_4 is octaalkylporphyrinogen (7), with R = Et or Pr, was prepared from $CrCl_2$(thf)$_2$ and orpg[Li(thf)]$_4$ [53]. The complexes are extremely air sensitive. They exhibit magnetic data consistent with a high-spin d^4 ground state. The crystal structure of the complex with R = Pr was obtained. The porphyrinogen adopts a saddle-shaped geometry. The Cr atoms sit slightly above the plane of the four pyrrole nitrogen atoms. The average Cr–N bond distance is 2.026(7) Å. The Li atoms are bound in η^5 fashion to opposite pyrroles on the same side of the macrocycle and each Li is further coordinated to two thf molecules. Exposure of [Cr(orpg)Li_2(thf)$_4$] to either N_2O or O_2 results in the formation of the Cr(IV) oxo species [(thf)(orpg)Cr(O)(thfLi)$_2$] (see Section 4).

7. Polynuclear complexes

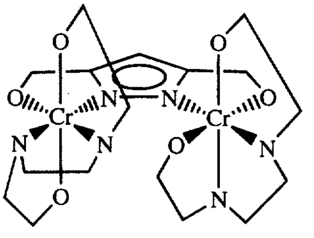
Reaction of L^8H_2 (**21**) and *trans*-[Cr(py)$_4F_2$]ClO_4 resulted in the formation of the dinuclear complex [CrL^8F]$_2$ [54]. A structural analysis of the bis-2-methoxyethanol solvate was made. The two *cis* fluoride ligands bridge the metal centers. A crystallographically imposed center of symmetry is in the centroid of the Cr_2F_2 ring. The ligands adopt a *cis,cis* N_2O_2 geometry. The Cr–N, Cr–O, and Cr–F distances are 2.065(1) and 2.039(1) Å, 1.891(1) and 1.929(1) Å, and 2.0172(8) and 1.9754(9) Å, respectively. The intramolecular Cr···Cr separation is 3.0787(4) Å. The F–Cr–F and Cr–F–Cr angles are 79.10(4)° and 100.90(4)°, respectively. Analysis of EPR, field dependent magnetization and magnetic susceptibility data was used to conclude that the Cr(III) centers are ferromagnetically coupled and that the complex has a septet ground state.



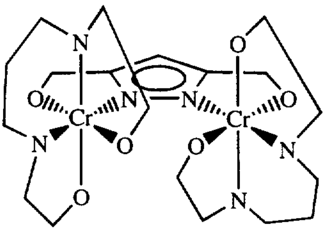
(21)

The synthesis and characterization of the dinuclear Cr(III) complexes $[Cr_2(tmpa)(\mu\text{-}O)(\mu\text{-}X)]^{n+}$, where tmpa is *tris*(2-pyridylmethyl)amine and $X = CO_3^{2-}$, $PhPO_4^{2-}$, and HS^-, were reported [55]. The crystal structure of $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}CO_3)Cr(tmpa)](ClO_4)_2$ was determined. The degree of antiferromagnetic coupling between Cr(III) centers is very dependent on the nature of the X bridging group. A strong correlation between oxo group basicity and degree of coupling was observed. The antiferromagnetic coupling constants for the new compounds vary from −30.4 to $-64\,cm^{-1}$. The structure of $[(tmpa)Cr(\mu\text{-}O)(\mu\text{-}CO_3)Cr(tmpa)](ClO_4)_2$ exhibits a Cr···Cr separation of 3.289(4) Å and an average Cr–N(py) bond distance of 2.072 Å. The Cr–N(amine), Cr–O(oxide), and Cr–O(CO_3) bond distances are 2.089(7) and 2.140(8) Å, 1.818(6) and 1.838(6) Å, and 1.924(7) and 1.934(7) Å. The Cr–O–Cr angle is 128.3(3)°.

A series of (diamine-N,N′-dicarboxylato)chromate(III) dinuclear complexes with the bridging ligand pyrazole-3,5-dicarboxylate, $pzdcH_3$ (**20**), was reported [56]. The diamine-*N,N′*-dicarboxylato ligands employed were $edda^{2-}$ and trimethylenediamine-*N,N′*-diacetate, $trdda^{2-}$. The crystal structures of $Na[Cr_2(edda)(\mu\text{-}pzdc)]\cdot 5H_2O$ and $Na[Cr_2(trdda)(\mu\text{-}pzdc)]\cdot 3H_2O$ were obtained. The complexes exhibit a Cr coordinated by the O,N,N,O tetradentate diaminedicarboxylate and N,O chelate of the $pzdc^{3-}$, which results in octahedral $Cr(N)_3(O)_3$ geometry. The $edda^{2-}$ complex has the structure shown in (**22**). The Cr···Cr distance is 4.473(3) Å. The Cr–O(pzdc) distances are 1.965(5) and 1.991(6) Å and the average Cr–O(edda) distance is 1.956(12) Å. The Cr–N(pzdc) distances are 2.051(7) and 2.030(6) Å and the average Cr–N(edda) distance is 2.063(17) Å. Temperature dependent magnetic susceptibility data reveal that the Cr(III) centers in $Na[Cr_2(edda)(\mu\text{-}pzdc)]\cdot 5H_2O$ exhibit weak ferromagnetic coupling ($2J = 1.21\,cm^{-1}$). A two-fold axis bisects the bridging $pzdc^{3-}$ ligand in $Na[Cr_2(trdda)(\mu\text{-}pzdc)]\cdot 3H_2O$, which displays a Cr···Cr distance of 4.560(4) Å. The symmetry independent Cr–O(pzdc) distance is 1.933(9) and the average Cr–O(trdda) distance is 1.94(1) Å. The Cr–N(pzdc) distance is 1.933(9) and the average Cr–N(trdda) distance is 2.055(7) Å.



(22)



(23)

Three Cr(III) dimers bridged by hydroxide and acetate groups were synthesized and subjected to magnetic characterization [57]. $[(tren)Cr(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)Cr(tren)](ClO_4)_4 \cdot 4H_2O$ and $[(trenH)Cr(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)_2Cr(trenH)](ClO_4)_5 \cdot 6H_2O$ were synthesized by reacting $[(tren)Cr(OH)(OH_2)]ClO_4$ with sodium acetate in a Cr/acetate ratio of 2 and 1, respectively. In the bis μ-acetato complex, the tren ligands are didentate, with the third pendant protonated, trenH. The complexes exhibit weak antiferromagnetic coupling with $J = -19.9$ and $-15.7\ cm^{-1}$ for the tren and trenH complexes, respectively. The synthesis and characterization was also reported for $[(H_2O)_4Cr(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)Cr(H_2O)_4](MesSO_3)_4 \cdot 8H_2O$. The complex was synthesized from glacial acetic acid, Cr(III) hydroxide dimer, and mesitylene-2-sulfonic acid. The Cr(III) atoms are weakly antiferromagnetically coupled with $J = -7.7\ cm^{-1}$. The crystal of the complex exhibits Cr–OH distances of 1.95(1) and 1.92(1) Å, Cr–O(carboxylate) distances of 1.94(1) and 1.93(2) Å, and Cr–OH_2 distances in the range 1.98–2.02 Å. The Cr–O–Cr angle is 133.1° and the Cr···Cr separation is 3.55(1) Å.

Reaction of potassium chromate with the ethyl ester of cysH, cysOEt, followed by neutralization with NaOH allowed the isolation of a complex with the formula $Na_2[Cr_2(O)_2(OH)_2(cysOEt)(cytOEt)Cl_2] \cdot H_2O$, where $cytH_2$ is the oxidized form of cys, cystine [58]. The room temperature magnetic moment is 5.42 μ_B. The complex exhibits a molar conductance of $99\ cm^2\ \Omega^{-1}\ mol^{-1}$. Experimental evidence suggests the absence of Cr–S coordination, coordination of NH_2 and the presence of Cr=O.

Photolysis of $[Cr(tacn)(ox)(N_3)]$ was found to result in the loss of 0.5 equiv. N_2 with the formation of mixed-valent, μ-nitrido-bridge $Cr^{III}Cr^{V}$ complex with the formulation $[Cr_2(\mu\text{-}N)(tacn)_2(ox)_2](N_3)$ [59]. The complex exhibits a $Cr^V{\equiv}N$ stretching band at $965\ cm^{-1}$ and a N_3 stretching band at $2073\ cm^{-1}$. The authors suggest a $Cr^V{\equiv}N{-}Cr^{III}$ linkage. Based on variable temperature magnetic susceptibility measurements, the complex exhibits an $S = 1$ ground state resulting from intramolecular antiferromagnetic coupling between Cr(V) ($S = 1/2$, d^1) and Cr(III) ($S = 3/2$, d^3).

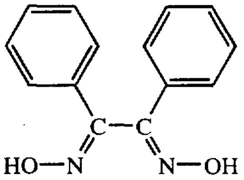
$[Cr_{12}S_{16}(PEt_3)_{10}]$ was synthesized and characterized by voltammetric and crystallographic techniques [60]. The dodecanuclear cluster was synthesized by reacting sulfur with $[Cr_6S_8(PEt_3)_6]$. The structure of the bis CH_2Cl_2 solvate consists of two octahedral Cr_6S_8 cores linked by two Cr–S bonds. The Cr···Cr distance between the Cr_6S_8 cores is 2.948(3) Å. The average Cr–Cr distance between the Cr involved in the inter-core link is 2.79 Å, whereas the average of the other Cr–Cr distances is 2.63 Å. Cyclic voltammetry data for $[Cr_6S_8(PEt_3)_6]$ exhibits an oxidation step at −0.86 V and reduction step at −1.54 V vs. ferrocene/ferrocenium. $[Cr_{12}S_{16}(PEt_3)_{10}]$ has two oxidation steps (−0.86 and −0.44 V) and two reduction steps (−1.57 and −2.12 V). The authors conclude that these waves correspond to a one-electron process occurring sequentially on the individual Cr_6S_8 cores.

The structure of the dihydrate of the 2,6-dihydroxybenzoate salt of the cation $[Cr_3(\mu_2\text{-}CH_3CO_2)_6(\mu_3\text{-}O)(H_2O)_3]^+$ was reported [61]. The complex has a triangular Cr_3O array with Cr–O–Cr angles within 0.5° of 120°. The coordination sphere of each octahedral Cr is comprised of the triply bridging oxygen and a *trans* water ligand in the axial sites, with the remaining sites occupied by oxygen atoms from the bridging acetates ligands. The Cr–(μ_3-O), Cr–OH_2, and Cr–O(acetato) distances are in the ranges 1.88–1.89 Å, 2.03–2.06 Å, and 1.96–2.00 Å, respectively. An extensive H-bonding network between the coordinated water and acetate ligands, waters of hydration and the counterion exists.

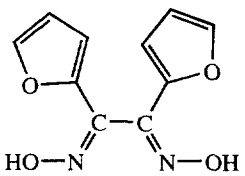
A study of the kinetics associated with the conversion of Cr(III) trimer to hexamer and monomer and trimer to tetramer in aqueous solution was performed [62]. The pH dependence studies were accounted for using a mechanism involving four and three pathways, respectively. The results suggest that pathways involving species with different nuclearities are preferred over those involving dimerization of individual oligomers.

The complexes $[Cr(cys)_2Cl]_2$, $[Cr(cyt)_2Cl]_2$ and $(NH_4)_2[CrCl_2(dtnb)_2]_2$, where cysH is cysteine, cytH is cystine, and dtnbH is dithiobisnitrobenzoic acid, were reported [63]. The complexes were synthesized from $CrCl_3py_3$ and the ligand. The products were characterized by IR, UV–vis, and spectroscopy. The magnetic moments are in the range 3.6–3.8 μ_B. The data are consistent with a lack of coordination of sulfur for the amino acid complexes. However, the dtnb complex does exhibit sulfur coordination. The authors suggest a structure with two bis(didentate ligand)Cr(III) ions bridged by two chloride ligands for the cys and cyt complexes. The dtnb complex has a proposed structure with either bridging chloride ligands or bridging dtnb ligands between the Cr(III) centers.

The hetero trinuclear dioxime complexes $[Cr(salen)Pd(dmg)_2Cr(salen)]$, $[Cr(salen)Pd(dpg)_2Cr(salen)]$, and $[Cr(salen)Pd(dfg)_2Cr(salen)]$, where $dpgH_2$ and $dfgH_2$ are (**24**) and (**25**), respectively [64], were prepared by refluxing a solution of $[Cr(salen)(H_2O)_2]NO_3$, $HC(OEt)_3$, and $Pd(dmg)_2$, $Pd(dpg)_2$ or $Pd(dfg)_2$. The complexes are nonelectrolytes and IR spectral analysis indicates that dioxime protons have been removed. The authors conclude that the oxime oxygen atoms coordinate to the Cr(salen) moiety, i.e. the $Pd(oxime)_2$ behaves as a didentate ligand to each of the Cr atoms, forming a bridge between the Cr centers. Magnetic data suggest that the electronic structure is best described as a Cr(III)–Cr(III) system with a small degree of antiferromagnetic coupling ($J = -3.38\ cm^{-1}$). The room temperature magnetic moment is 5.12 μ_B.



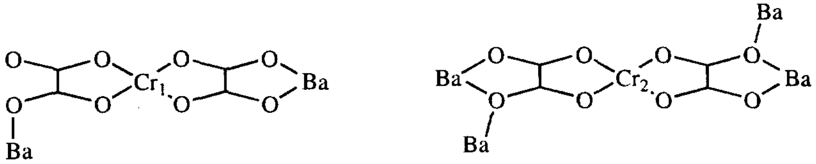
(24)



(25)

The kinetics for the formation of $[Cr(H_2O)_4(OH)]_2Mo(CN)_8$ from $[Cr(OH)(H_2O)_5]^{2+}$ and $[Mo(CN)_6]^{4-}$ were examined [65]. The product stoichiometry was determined using the method of continuous variations and the mole ratio method. The bridging in the product is of the form Mo–C≡N–Cr. Activation parameters were reported. The rate of reaction is pH dependent, decreasing with a decrease in pH. The proposed mechanism includes a slow addition of the first Cr moiety with loss of a water ligand (outer-sphere association followed by an I_a process) and a fast addition of the second.

A detailed analysis was carried out of the Mössbauer spectra for the complexes $[(tacn)Cr(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2Fe(tacn)](ClO_4)_2$, $[(tacn)Cr(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2Fe(tacn)](PF_6)_2$, and $[(tacd)Cr(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2Fe(tacd)](PF_6)_2$, where tacd is triazacyclododecane [66]. Spectra were analyzed as a function of field strength and temperature. The μ-OH complex has Fe^{2+} ($S=2$) and Cr^{3+} ($S=3/2$) ions which exhibit antiferromagnetic coupling resulting in an effective $S=1/2$. The μ-O complexes have Fe^{3+} ($S=5/2$) and Cr^{3+} ($S=3/2$) ions which exhibit antiferromagnetic coupling resulting in an effective $S=1$ state. The coupling between metal centers is much greater for the μ-O complexes than that observed in the μ-OH complex. The quadrupole splitting $\Delta E_Q = -2.00$ mm/s at 4.2 K exhibited by the μ-O complexes is unusually large. The observed relaxation for the Fe^{2+}, Cr^{3+} and Fe^{3+}, Cr^{3+} pairs is faster than that observed for diiron pairs.

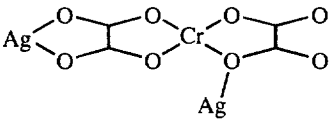


(26)

The crystal structures of the complexes resulting from the self-assembly of $[Cr(bpy)(ox)_2]^-$ with Ba(II), Mn(II), Co(II) were reported [67]. The two Cr atoms in $[BaCr_2(bpy)_2(\mu\text{-}ox)_2(H_2O)]_n \cdot nH_2O$ are in different environments. The two oxalato groups bonded to the first Cr exhibit different coordination modes, as shown in (**26**). Each Ba atom is connected to two Cr1 units forming an infinite 2D sheet. The sheets are linked together through a pillar formed by two Ba(II) connected by four oxalato bridges coming from four Cr2 moieties, which together form an extended 2D sheet. Reaction of $[BaCr_2(bpy)_2(\mu\text{-}ox)_2(H_2O)]_n \cdot nH_2O$ with $MnSO_4 \cdot 4H_2O$

or $CoSO_4 \cdot 7H_2O$ results in the formation of $[MnCr_2(bpy)_2(\mu\text{-}ox)_4]_n$ or $[CoCr_2(bpy)_2(\mu\text{-}ox)_2(ox)_2(H_2O)_2] \cdot H_2O$, respectively. $[MnCr_2(bpy)_2(\mu\text{-}ox)_4]_n$ displays an asymmetric unit composed of $MnCr_2(bpy)_2(\mu\text{-}ox)_4$. The Mn atom exhibits a flattened, square-antiprism coordination geometry comprised of four bridging ox^{2-} ligands. Each of the Cr atoms in the asymmetric unit possesses an octahedral coordination geometry made up of a bpy and two didentate ox^{2-} ligands bridging Mn(II) centers. The system consists of infinite heterobimetallic chains formed of diamond-shaped units sharing the Mn atoms and with the Cr atoms in the other two sites. The Cr···Mn distances range from 5.533 to 5.573 Å. The average Cr–O and Cr–N distances are 1.97(4) Å and 2.05(1) Å. The structure of $[CoCr_2(bpy)_2(\mu\text{-}ox)_2(ox)_2(H_2O)_2] \cdot H_2O$ is composed of discrete Cr_2Co units. The Co(II) ion is on an inversion center, coordinated to *trans* water ligands and two bridging ox^{2-} ligands. The Cr(III) coordination geometry is octahedral with the remainder of the coordination sphere comprised of the bpy and terminal oxalate ligands. The Cr···Co distance is 5.288 Å. The average Cr–Ox(bridge) and Cr–Ox(terminal) distances are 1.946(7) Å and 1.99(18) Å, respectively. The average Cr–N distance is 2.056(4) Å.

A similar approach, employing the reaction of $[BaCr_2(bpy)_2(\mu\text{-}ox)_2(H_2O)_2] \cdot H_2O$ or $K[Cr(bpy)(ox)_2] \cdot 4H_2O$ and $Cu(NO_3)_2 \cdot 4H_2O$ or Ag_2SO_4, resulted in the formation of $[CuCr_2(bpy)_2(\mu\text{-}ox)_2(ox)_2(H_2O)_2] \cdot 1.5H_2O$ and $AgCr(bpy)_2(\mu\text{-}ox)_2(H_2O)_2$ [68]. The Cu(II) complex consists of discrete trinuclear units. The coordination about Cu exhibits considerable tetragonal distortion. The coordination sphere consists of two *trans* water ligands and two bridging oxalato ligands. The Cr coordination sphere is similar to that found in the analogous $CoCr_2$ complex (vide supra). The average Cr–Ox(terminal), Cr–Ox(bridge), Cr–N distances are 1.946(1) Å, 1.978(6) Å, and 2.042(16) Å, respectively. The complex exhibits an $S=5/2$ ground state and an antiferromagnetic coupling constant of $J=-18.8\ cm^{-1}$. The structure of $AgCr(bpy)_2(\mu\text{-}ox)_2(H_2O)_2$ consists of discrete Cr_2Ag_2 units with the metal atoms linked by four bridging oxalate ligands. The coordination, as seen in (**27**), is atypical: two of the oxalato ligands exhibit normal tetradentate coordination, but the other two coordinate with three oxygen atoms. The Ag atoms are five-coordinate (distorted trigonal bipyramidal) with three oxygen atoms from oxalate ligands and two water molecules making up the coordination sphere. The coordination sphere of the Cr(III) is as described for $[CuCr_2(bpy)_2(\mu\text{-}ox)_2(ox)_2(H_2O)_2] \cdot 1.5H_2O$ with average Cr–Ox(terminal), Cr–Ox(bridge), Cr–N distances of 1.950(7) Å, 1.975(7) Å, and 2.052(6) Å, respectively. The short Cr···Ag distances are 3.841 Å and 3.886 Å.



(**27**)

The structure of the complex with the formula $[Fe^{II}(bpy)_3]_n^{2+}[AgCr^{III}(ox)_3]_n^{2n-}$ was reported [69]. The polymeric anion is composed of a dimetal–oxalate network with the cations in the voids of the framework. The anion subunits and the cations exhibit the Λ configuration. All Cr(III) ions are coordinated to three oxalato ligands that each bridge to a Ag(I) ion, which in turn exhibits tris(oxalato) coordination. The result is a chiral polymeric decagon framework. The crystallographically unique Cr–O distances are 1.936(5) Å and 1.947(5) Å.

Diffusion of $[Cr(ox)_3]^{3-}$ and Mn^{2+} into a solution of $(TTF)_3(BF_4)_2$, where TTF is the tetrathiafulvalene, resulted in the formation of the complex $(TTF)_4\{Mn(H_2O)_2[Cr(ox)_3]_2\}\cdot 14H_2O$ [70]. The material crystallizes with linear Cr–Mn–Cr trimers in which the Mn resides on an inversion center. The two $Cr(ox)_3$ units are bridged by the oxalato ligands. The coordination sphere of the octahedral Mn is completed by water ligands. The trimers are linked via a H-bonding network to form a 2D framework. The ground state of the system is $S=11/2$, with a ferromagnetic coupling constant $J=0.54\ cm^{-1}$.

A series of five complexes containing chelating or bridging *cis*-$[Cr(OH)_2(en)_2]^+$ units and zinc or cadmium was prepared and characterized by X-ray crystallography [71]. $[ZnCl_2(\mu\text{-}OH)Cr(en)_2(\mu\text{-}OH)][ClO_4]_n$ forms chains. The tetrahedral $Zn(\mu\text{-}OH)_2Cl_2$ units bridge Cr centers. The average Cr–O and Cr–N distances are 1.94 Å and 2.10 Å, respectively. The complex $[\{ZnCl_2(\mu\text{-}OH)Cr(en)_2(\mu\text{-}OH)\}_2]Cl_2$ exhibits a structure with discrete "squares" formed by diagonal Cr and Zn atoms. The average Cr–O and Cr–N distances are 1.958 Å and 2.078 Å, respectively. $[Cd_3(\mu\text{-}Cl)_4Cl_4\{Cr(\mu_3\text{-}OH)(\mu\text{-}OH)(en)_2\}_2]\cdot 4H_2O$ has three octahedral Cd atoms. The central Cd resides on an inversion center and shares opposite triangular faces with the two end Cd coordination spheres. The crystallographically unique Cr is bridged to a terminal Cd by one of its OH^- ligands. The other hydroxide ligand is part of a triangular face shared by the central and terminal Cd atoms. The Cr–(μ-OH) and Cr–(μ$_3$-OH) distances are 1.925(2) Å and 1.981(2) Å, respectively. The average Cr–N distance is 2.086 Å. $[[Cd(\mu\text{-}Cl)(H_2O)_2\{Cr(\mu\text{-}OH)_2(en)_2\}](ClO_4)$ crystallizes with infinite chains of octahedrally coordinated Cd atoms bridged by chloride ligands. The coordinated Cr complex ligands are arranged in 2_1 fashion along the chain. The average Cr–O and Cr–N distances are 1.967 Å and 2.090 Å. The final compound, $[Cd_2(\mu\text{-}Cl)_2Cl_3(H_2O)_3\{Cr(\mu\text{-}OH)_2(en)_2\}]_n$, also adopts a polymeric structure. However, in this compound, the *cis*-$[Cr(OH)_2(en)_2]^+$ ligands are coordinated to every other Cd in a chain of octahedrally coordinated Cd atoms bridged by chloride ligands. The average Cr–O and Cr–N distances are 1.91 Å and 2.06 Å.

The complexes $\{M(II)[Cr(III)(ap)_3]_2\}Cl_2$, where M = Zn, Ni and Cu and ap is 3-amino-1-propanol, were reported [72]. Based on IR and UV–vis spectroscopy; conductivity, magnetic and thermal differential analysis studies; and by X-ray powder diffraction of hydrolysis products, the structures were assigned. The data are consistent with the M(II) bridging the two Cr(III) ions via shared edges of the octahedra.

The reaction of $CrCl_3$ or $CrBr_2$, Cr_2O_3, elemental Cr, and SiO_2 was used to isolate the complexes $Cr_4(Si_2O_7)X_2$ (X = Cl, Br) [73]. The complexes crystallize with eight crystallographically unique Cr(II) ions. Two of the Cr(II) ions have a coordination sphere of CrO_5X (distorted octahedral), one with CrO_3X_3 (distorted *mer*-octahedral), three with CrO_3X_2 (distorted trigonal bipyramidal, axial halides, square plane of oxygens with one corner missing) and two with CrO_4X (square pyramidal, apical halide). Jahn–Teller distortion is clearly visible in the observed coordination geometries. The average Cr–O(short) and Cr–O(long), and Cr–X distances are 2.057 Å, 2.527 Å, and 2.694 Å for the chloride complex and 2.068 Å, 2.433 Å, and 2.798 Å for the bromide complex.

A series of heterobimetallic μ-nitrido porphyrin complexes was reported [74]. Reaction of NRe(OEP) and ClCr(TPP) results in the formation of a nitrido bridge species. The stoichiometry of the product is 1:1 and the equilibrium constant was determined to be $3.8(0.2) \times 10^5\ M^{-1}$. The NRe(OEP) and ClCr(TTP) or ClCr(OEP) systems were also examined and gave similar results. The proposed mechanism for bimetallic complex formation involves initial loss of the chloride ligand.

References

[1] P.A. Lorenzo Luis, P. Martin-Aaraz, P. Gili, C. Ruis-Pérez, M. Hernández-Molina, X. Solans, Acta Crystollogr. C52 (1996) 1441.
[2] H.-T. Chiu, Y.-P. Chen, S.-H. Chuang, J.-S. Jen, G.-H. Lee, S.-M. Peng, Chem. Commun. (1996), 139.
[3] M. Torrent, P. Gili, M. Duran, M. Solá, J. Chem. Phys. 104 (1996) 9499.
[4] S.L. Brauer, A.S. Hneihen, J.S. McBride, K.E. Wetterhahn, Inorg. Chem. 35 (1996) 373.
[5] P. Lay, A. Levina, Inorg. Chem. 35 (1996) 7709.
[6] A. Niemann, U. Bossek, G. Haselhorst, K. Wieghardt, B. Nuber, Inorg. Chem. 35 (1996) 906.
[7] K.D. Sugden, K.E. Wetterhahn, Inorg. Chem. 35 (1996) 651.
[8] K.D. Sugden, K.E. Wetterhahn, Inorg. Chem. 35 (1996) 3727.
[9] R. Bose, B. Fonkeng, G. Barr-David, R.P. Farrell, R.J. Judd, P.A. Lay, D.F. Sangster, J. Am. Chem. Soc. 118 (1996) 7139.
[10] A. Bakac, W.-D. Wang, J. Am. Chem. Soc. 118 (1996) 10325.
[11] D.M. Hankin, A.A. Danopoulos, G. Wilkinson, T.K.N. Sweet, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1996) 4063.
[12] R. Jin, C.S. Cho, L.H. Jiang, S.C. Shim, Bull. Korean Chem. Soc. 17 (1996) 657.
[13] M. Dionne, J. Jubb, H. Jenkins, S. Wong, S. Gambarotta, Inorg. Chem. 35 (1996) 1874.
[14] R.D. Köhn, G. Kociok-Köhn, M. Haufe, Chem. Ber. 129 (1996) 25.
[15] D.A. House, J. Wang, A. Derwahl, Inorg. Chim. Acta 248 (1996) 93.
[16] P. Riccieri, E. Zinato, Inorg. Chem. 35 (1996) 974.
[17] R. Mettendorf, R. Buchem, K.-F. Tebbe, F. Wasgestian, J. Lober, Inorg. Chim. Acta 245 (1996) 17.
[18] C.R.A. Rajendram, P.E. Hoggard, Trans. Met. Chem. 21 (1996) 61.
[19] M. Brorson, C.J.H. Jacobsen, C.M. Jensen, I. Schmidt, J. Villadsen, Inorg. Chim. Acta 247 (1996) 189.
[20] S. Díaz-Moreno, A. Muñoz-Páez, J.M. Martínez, R.R. Pappalardo, E. Sánchez Marcos, J. Am. Chem. Soc. 118 (1996) 12654.
[21] A. Bleuzen, F. Foglia, E. Furet, L. Helm, A.E. Merbach, J. Weber, J. Am. Chem. Soc. 118 (1996) 12777.
[22] Kabir-ud-Din, G.J. Khan, Z. Khan, Md.Z.A. Rafiquee, J. Chem. Res. (S) (1996) 178.
[23] A. Zhitkovish, V. Voitkun, M. Costa, Biochemistry 35 (1996) 7275.
[24] H.M. Chawla, U. Hooda, V. Singh, Synth. React. Inorg. Met.-Org. Chem. 26 (1996) 775.
[25] H. Kanno, J. Yamamoto, S. Utsuno, J. Fujita, Bull. Chem. Soc. Jpn. 69 (1996) 665.

[26] H. Drevs, A. Schmeißer, H. Hartung, U. Baumeister, Chem. Ber. 129 (1996) 853.

[27] T. Schönherr, M. Atanasov, A. Hauser, Inorg. Chem. 35 (1996) 2077.

[28] J.I. Sachinidis, R.D. Shalders, P.A. Tregloan, Inorg. Chem. 35 (1996) 2497.

[29] A. Katafias, P. Kita, Pol. J. Chem. 70 (1996) 1579.

[30] R. Nakata, M. Yano, Y. Ochi, N. Hatanaka, H. Oki, Bull. Chem. Soc. Jpn. 69 (1996) 1261.

[31] T.M. Santos, J.D. Pedrosa de Jesus, F.M.L. Amado, P.M. Domingues, M.G. Sanatana-Margues, A.J. Ferrer-Correia, Polyhedron 15 (1996) 2887.

[32] M.S. El-Shahawi, Spectrochim. Acta A52 (1996) 139.

[33] T.-B. Wen, J.-C. Shi, Q.-T. Liu, B.-S. Kang, B.-M. Wu, T.C.W. Mak, Acta Crystallogr. C52 (1996) 1204.

[34] T. Fujihara, T. Schönherr, S. Kaizaki, Inorg. Chim. Acta 249 (1996) 135.

[35] S.J. Brudenell, S.J. Crimp, J.K.E. Higgs, B. Moubaraki, K.S. Murray, L. Spiccia, Inorg. Chim. Acta 247 (1996) 35.

[36] M. Maskus, H.D. Abruña, Langmuir 12 (1996) 4455.

[37] A.-M.M. Abdel-Mawgoud, Trans. Met. Chem. 21 (1996) 219.

[38] K. Langemann, D. Heineke, S. Rupprecht, K.N. Raymond, Inorg. Chem. 35 (1996) 5663.

[39] S.P. Kaiwar, A. Sreedhara, M.S.S. Raghavan, C.P. Rao, V. Jadhav, K.N. Ganesh, Polyhedron 15 (1996) 765.

[40] G. Galsbøl, C.H. Petersen, K. Simonsen, Acta Chem. Scand. 50 (1996) 567.

[41] T. Beissel, T. Glaser, F. Kesting, L. Wieghardt, B. Nuber, Inorg. Chem. 35 (1996) 3936.

[42] A. Sokolowski, E. Bothe, E. Bill, T. Weyhermüller, K. Wieghardt, Chem. Commun. (1996) 1671.

[43] C.J. Carrano, H. Drechsel, D. Kaiser, G. Jung, B. Matzanke, G. Winkelmann, N. Rochel, A.M. Albrecht-Gary, Inorg. Chem. 35 (1996) 6430.

[44] C.L. Beswick, R.D. Shalders, T.W. Swaddle, Inorg. Chem. 35 (1996) 991.

[45] S. Sievertsen, B. Aßmann, H. Homborg, Z. Anorg. Allg. Chem. 622 (1996) 1685.

[46] R.A. Palmer, B.S. Potter, S. Tanriverdi, J.N. Lisgarten, C.D. Flint, D.M. Gazi, Acta Crystallogr. C52 (1996) 1177.

[47] M. Dionne, J. Jubb, H. Jenkins, S. Wong, S. Gambarotta, Inorg. Chem. 35 (1996) 1874.

[48] K.B. Hansen, J.L. Leighton, E.N. Jacobsen, J. Am. Chem. Soc. 118 (1996) 10924.

[49] S.S. Mandal, N.V. Kumar, U. Varshney, S. Bhattacharya, J. Inorg. Biochem. 63 (1996) 265.

[50] N. Sakagami, M. Nakahanada, K. Ino, A. Hioki, S. Kaizaki, Inorg. Chem. 35 (1996) 683.

[51] A. Niemann, U. Bossek, G. Haselhorst, K. Wieghardt, B. Nuber, Inorg. Chem. 35 (1996) 906.

[52] T. Miekisch, H.J. Mai, R. Meyer zu Köcker, K. Dehnicke, J. Magull, H. Goesmann, Z. Anorg. Allg. Chem. 622 (1996) 583.

[53] M. Dionne, J. Jubb, H. Jenkins, S. Wong, S. Gambarotta, Inorg. Chem. 35 (1996) 1874.

[54] R. Sanzenbacher, A. Böttcher, H. Elias, M. Hüber, W. Haase, J. Glerup, T.B. Jensen, M. Neuburger, M. Zehnder, J. Springborg, C.E. Olsen, Inorg. Chem. 35 (1996) 7493.

[55] N.K. Dalley, X. Kou, C.J. O'Connor, R.A. Holwerda, Inorg. Chem. 35 (1996) 2196.

[56] N. Sakagami, M. Nakahanada, K. Ino, A. Hioki, S. Kaizaki, Inorg. Chem. 35 (1996) 683.

[57] S.J. Brudenell, S.J. Crimp, J.K.E. Higgs, B. Moubaraki, K.S. Murray, L. Spiccia, Inorg. Chim. Acta 247 (1996) 35.

[58] S.P. Kaiwar, A. Sreedhara, M.S.S. Raghavan, C.P. Rao, V. Jadhav, K.N. Ganesh, Polyhedron 15 (1996) 765.

[59] A. Niemann, U. Bossek, G. Haselhorst, K. Wieghardt, B. Nuber, Inorg. Chem. 35 (1996) 906.

[60] S. Kamiguchi, H. Imoto, T. Saito, Chem. Lett. (1996) 555.

[61] T. Glowiak, H. Kozlowski, L.S. Erre, G. Micera, Inorg. Chim. Acta 248 (1996) 99.

[62] A. Drljaca, L. Spiccia, Polyhedron 15 (1996) 2875.

[63] M.S. El-Shahawi, Spectrochim. Acta A52 (1996) 139.

[64] S.-W. Zhang, D.-Z. Liao, Z.-H. Jiang, G.-L. Wang, Trans. Met. Chem. 21 (1996) 166.

[65] S.I. Ali, S. Sharma, Z. Khan, Trans. Met. Chem. 21 (1996) 222.

[66] H.H. Rodriquez, Y.-M. Xia, P.G. DeBrunner, P. Chaudhuri, K. Wieghardt, J. Am. Chem. Soc. 118 (1996) 7542.

[67] F.D. Rochon, R. Melanson, M. Andruh, Inorg. Chem. 35 (1996) 6086.

[68] M. Andruh, R. Melanson, C.V. Stager, F.D. Rochon, Inorg. Chim. Acta 252 (1996) 309.

[69] H.W. Schmalle, R. Pellaux, S. Decurtins, Z. Kristallogr. 211 (1996) 533.

[70] E. Coronado, J.R. Galán-Mascarós, C. Giménez-Saiz, C.J. Gómez-García, C. Ruiz-Pérez, S. Triki, Adv. Mater. 8 (1996) 737.

[71] F. Rominger, U. Thewalt, Z. Naturforsch. 51 (1996) 1716.

[72] I. Jitaru, C.I. Lepadatu, C. Guran, M. Brezeanu, Rev. Roum. Chim. 41 (1996) 171.

[73] A. Schmidt, R. Glaum, J. Beck, J. Solid State Chem. 127 (1996) 331.

[74] C. Tong, L.A. Bottomley, Inorg. Chem. 35 (1996) 5108.