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Preparation, Characterization, Mössbauer Spectra, and Electron Spin Resonance Spectra of Iron(II) and Iron(III) Complexes of the Dithiolate Cyclopentadienedithiocarboxylate

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The preparation of tetraethylammonium salts of bis(cyclopentadienedithiocarboxalato)ferrate(II) and tris(cyclopentadienedithiocarboxalato)ferrate(III) is reported. Both complexes exhibit high-spin behavior. The Mössbauer spectrum of the iron(II) complex is characterized by IS = 0.69 mm/s (metallic iron reference) and ΔE_q = 4.52 mm/s at 78 K. The large quadrupole splitting is rationalized by the apparent five-coordination at the Fe(II) ion in the solid state. The observation of a temperature-independent magnetic moment in the iron(III) complex allows the placement of the cyclopentadienedithiocarboxylate ligand in the spectrochemical series of dithiolate ligands. The Mössbauer spectrum of the iron(III) complex is characterized by IS = 0.41 mm/s (broad singlet with Γ of 1.71 mm/s) at 78 K. The electron spin resonance spectrum of the iron(III) complex exhibits g = 9.30, 4.31, and 0.77, characteristic of a large zero-field splitting of the $^6S_{5/2}$ system.

Introduction

The tremendous interest which has been generated in the study of iron–sulfur enzymatic systems[2,3] makes the study of iron–sulfur complexes of varying oxidation states and chemical environments of particular importance. While a large body of work exists on iron(III) 1,2-dithiolene and 1,1-dithiolate complexes, the majority are low spin in nature. Iron(II) complexes are known but their occurrence is rare.[4] In particular, aliphatic and aromatic iron(II) dithiolates are unknown.[5] Our interest in the effect of the cyclopentadienedithiocarboxylate ($cpdt^{2-}$) ligand coupled with the large accumulation of knowledge on iron dithiolate complexes prompted our investigation of Fe–$cpdt^{2-}$ systems so that comparisons could be made.

Experimental Section

Materials. Acetonitrile was repeatedly distilled from phosphorus pentoxide. Anhydrous $FeBr_2$ and $FeCl_3$ were purchased from Research Organic-Inorganic Chemical Corp. Anhydrous $(C_2H_5)_4NCl$ and $(C_2H_5)_4NBr$ were obtained from Aldrich Chemical Co.

The disodium salt of cyclopentadienedithiocarboxylic acid, $Na_2S_2CC_5H_4$, was prepared as previously reported.[6]

$[(C_2H_5)_4N]_2Fe(C_5H_4CS_2)_2$. Typically, 0.613 g of $FeBr_2$ was dissolved in anhydrous degassed acetonitrile. The resulting solution was frozen and both 1.555 g of $Na_2S_2CC_5H_4$ and 1.138 g of $(C_2H_5)_4NBr$ were added. The resulting mixture was allowed to thaw slowly while stirring. After the resulting brown solution had stirred for 2 h at room temperature, NaBr was removed by filtration. The filtrate was reduced in volume under vacuum and the bright red product was removed by further filtration. Anal. Calcd for $[(C_2H_5)_4N]_2Fe(C_5H_4CS_2)_2$: C, 56.35; H, 8.11; N, 4.69. Found: C, 56.44, H, 8.03; N, 4.74.

$[(C_2H_5)_4N]_3Fe(C_5H_4CS_2)_3$. This air-sensitive brown complex was prepared in the same manner as the iron(II) complex above. Typical starting ratios were 0.7002 g of $FeCl_3$, 3.3233 g of $Na_2S_2CC_5H_4$, and 2.189 g of $(C_2H_5)_4NCl$. Anal. Calcd for $[(C_2H_5)_4N]_3Fe(C_5CS_2)_3$: C, 58.16; H, 8.31; N, 4.85; S, 22.18. Found: C, 57.65; H, 8.44; N, 4.66; S, 21.53.

Analysis. All analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

Methods. Reactions, filtrations, transfers, etc. were carried out in as rigorously anhydrous (nitrogen) an atmosphere as could be maintained employing Schlenk-tube techniques.[6] Both compounds of iron were *very* air sensitive and decomposed to a black material almost instantaneously when exposed to the atmosphere.

Magnetic Susceptibility Determinations. Magnetic susceptibilities were carried out on solid samples using the Gouy method and $Hg[Co(SCN)_4]$ as a calibrant. Pascal's constants were used to correct for diamagnetic contributions from the ligand, the cation, and the core electrons of the metal.[7] Measurements made at other than ambient room temperature employed a Dewar assembly and liquid nitrogen–solvent slushes or liquid nitrogen as coolant.

Spectroscopic Measurements. Mössbauer spectra were obtained using an Austin Science Associates, Inc., spectrometer equipped with a "fast data accumulation package" electronics system. A Nuclear Data Model 2200 multichannel analyzer was used for data collection and storage. Data were transmitted via a teletype terminal into a PDP-10 computer for data reduction. A least-squares fit, assuming Lorentzian line shapes, was performed for each spectrum. Velocity calibration was done by laser interferometry and all spectra were referenced to an iron foil standard with the midpoint of the iron spectrum assigned an isomer shift value of 0.00 mm/s. Samples run at room temperature and at 4.2 K had source and absorber at the same temperature. Samples run at Dry Ice–acetone and liquid nitrogen temperatures had the source at room temperature. No second-order Doppler correction was made in the data reported.

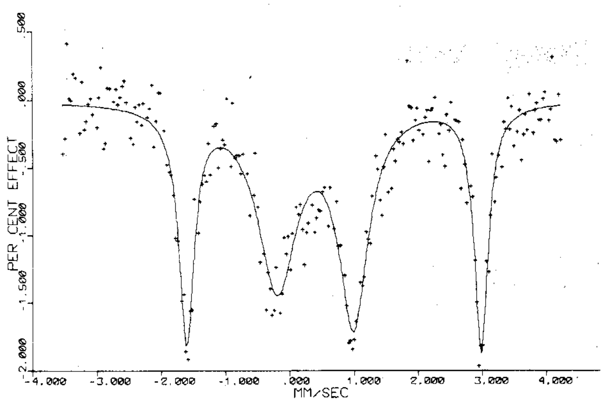

Figure 1. Mössbauer spectrum of $[(C_2H_5)_4N]_2Fe(C_5H_4CS_2)_2$. Inner doublet is due to an Fe(III) decomposition product.

Table I. Mössbauer Parameters of $[(C_2H_5)_4N]_2Fe(C_5H_4CS_2)_2$

Temp, K	Inner peaks		Outer peaks	
	IS, mm/s	ΔE_q, mm/s	IS, mm/s	ΔE_q, mm/s
295	0.34 ± 0.02	1.09 ± 0.01	0.62 ± 0.01	4.56 ± 0.02
78	0.40 ± 0.01	1.20 ± 0.01	0.69 ± 0.01	4.52 ± 0.02
4.2	0.31 ± 0.02	1.27 ± 0.02	0.59 ± 0.01	4.65 ± 0.01

Mössbauer samples were loaded into special plastic petri dish type holders (2.54 cm in diameter) which contained paraffin in one side. The powdered sample was poured evenly over the half without paraffin and the two sides were pressed together to give a sample mounted on a layer of wax. Typically, samples ranged from 100 to 400 mg. The iron(III) complex was loaded in a glovebag. Due to its exteme sensitivity, the iron(II) sample was prepared in a drybox. Even under these conditions there was some darkening of the iron(II) compound. After loading, the sample containers were sealed with parafilm and placed in glass tubes which were evacuated for shipment. ESR spectra were obtained as before.[6]

Results and Discussion

Tetraethylammonium bis(cyclpentadienedithiocarboxylato)ferrate(II) is an extremely air-sensitive red complex. Slight decomposition to yield a brown product occurred in all attempts to handle the compound using Schlenk techniques. Of the other reported iron(II) dithiolate complexes, only the bis(*N*,*N*-diethyldithiocarbamato)iron(II) complex does not undergo autoxidation when iron(II) salts are employed as the starting materials in the syntheses.[5,8] The cyclopentadienedithiocarboxylate complex exhibits a magnetic moment of 4.83 BM which is indicative of a high-spin iron(II) system without spin–orbit interaction.[7] A representative Mössbauer spectrum of the complex is shown in Figure 1 and the Mössbauer data are given in Table I. The parameters are seen to be temperature independent. All samples of the complex prepared for Mössbauer spectroscopy showed four peaks. The outer two peaks have parameters which are consistent with high-spin iron(II); the inner two peaks correspond to iron(III).[9] It was found that if insufficient care were taken in storing the Mössbauer sample or if the complex were exposed to air, the outer peaks disappeared and only the inner two lines remained. The inner lines are thus assigned to an iron(III) decomposition product since they did not change in appearance with extended atmospheric exposure.

Although the isomer shift of the outer doublet in Figure 1 is typical of high-spin Fe(II), the quadrupole splitting of ca. 4.56 mm/s is unusually large. There are at least four other Fe(II) systems reported to have such large quadrupole splitting parameters, two of which are reported to contain pentacoordinate Fe(II).[10–13] The dimeric unit *N*,*N*-diethyldithiocarbamatoiron(II) has the Mössbauer parameters listed in Table II.[10] X-ray powder spectra have indicated that the iron(II) dithiocarbamate system is square pyramidal with the sulfur of a second $[(C_2H_5)_2NCS_2]_2Fe$ unit in the apical position.[8] A molecular orbital calculation gave the relative ordering $d_{x^2-y^2} < d_{xz} < d_{yz} < d_{z^2} < d_{xy}$, which is also in agreement with the ordering expected for square-pyramidal geometry.[10]

Table II. Mössbauer Parameters for $\{[(C_2H_5)_2NCS_2]_2Fe\}_2$

Temp, K	IS, mm/s	ΔE_q, mm/s
300	1.02	4.01
100	1.16	4.16

Table III. Mössbauer Data for $[(C_2H_5)_4N]_3Fe(C_5H_4CS_2)_3$

Temp,	One-line fit		Two-line fit	
	IS, mm/s	Line width, mm/s	IS, mm/s	ΔE_q, mm/s
295	0.41	0.98	0.41	0.52
195	0.41	1.13	0.42	0.59
78	0.41	1.71	0.47	0.51
4.2	Spectra magnetically split into six lines			

A detailed study of another Fe(II) system, bis(5,5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazocyclotetradeca-1-(14),7-dione)iron(II) perchlorate, yielded a Mössbauer spectrum with a quadrupole splitting of 4.0 mm/s.[11] This system again contains pentacoordinate Fe(II) in a square-pyramidal structure with the iron slightly out of the basal plane and the perchlorate ion in the apical position. While the optical spectrum of bis(thiosemicarbazide)iron(II) [ΔE_q = 4.65 s^{-1} (300 K)] has been rationalized in terms of a distorted octahedron,[13] the arguments presented for the structural assignment do not rigorously preclude a five-coordinate system. Unfortunately, the above examples not withstanding the large quadrupole splitting value does not allow the unequivocal assignment of pentacoordination since the eight-coordinate 1,8-naphthyridine complex of Fe(II) exhibits a ΔE_q value of 4.54 mm/s.[12]

For high-spin iron(II) systems, the isomer shift has been related to the nephelauxtic effect of the ligand to which the ion is coordinated.[9] Since the nephelauxtic effect corresponds to the fractional reduction of the interelectronic repulsion parameters in a complex relative to those of the free ion, it can be related to the expansion of the valence orbitals in the complex. This expansion of the valence d orbitals in iron should result in decreased shielding of the s electrons and a corresponding increase in s-electron density at the nucleus. Thus the lower value for the isomer shift (concomitant with greater s-electron density at the iron nucleus) exhibited by the cyclopentadienedithiocarboxylato complex as compared to the value for the bis(*N*,*N*-diethyldithiocabamato)iron(II) is evidence of the greater electron-withdrawing ability of the $cpdt^{2-}$ ligand.

The brown, air-sensitive tetraethylammonium tris(cyclopentadienedithiocarboxylato)ferrate(III) exhibits a room-temperature magnetic moment of 5.93 BM which corresponds to the expected spin-only moment of high-spin d^5 systems. The magnetic moment remains constant between 77 and 300 K. As anticipated, only peaks due to the ligand could be observed in the optical spectrum.

The Mössbauer spectra for the Fe(III) compound (Figure 2 and Table III) are consistent with a high-spin, slightly distorted, octahedral system.[14] A broadened, temperature-independent singlet is observed between 295 and 78 K. The spectrum is magnetically split into the usual symmetric six-line pattern at 4.2 K. This magnetic hyperfine is a result of slow-spin relaxation in the complex at low temperature and is commonly exhibited by high-spin Fe(III) systems having large organic ligands.[14] The small quadrupole splitting, exhibited as line broadening at temperatures above 78 K, is probably due to some small amount of mixing-in of the $^6A_1$ and $^2T_2$ states via the $^4T_1$ state which causes the energy

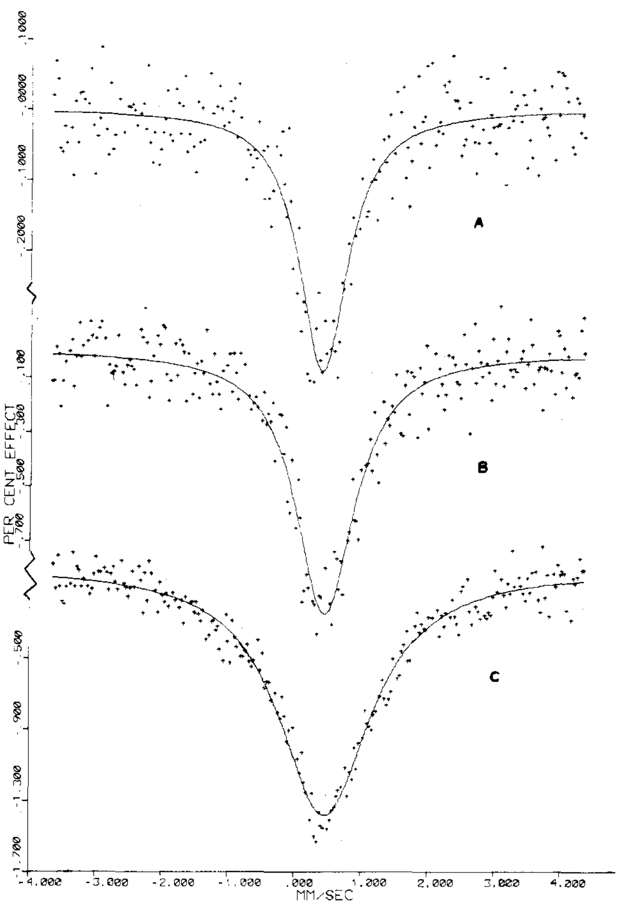

Figure 2. Mössbauer spectrum of $[(C_2H_5)_4N]_3Fe(C_5H_4CS_2)_3$: A, 295 K; B, 195 K; C, 78 K.

levels to split and repel each other as a result of a small reduction from cubic symmetry.

The observation of high-spin behavior for the Fe^{III}–$cpdt^{2-}$ complex allows the placement of the cyclopentadienedithiocarboxylate ligand in the spectrochemical series of other dithiolate ligands. For the 1,1-dithiolates of iron(III), the spectrochemical series is[15-17] $dtp^- < dtc^- < dtx^- < dtb^- < dta^-$, where dtp^- = dithiophosphate, $(RO)_2PSS^-$; dtc^- = dithiocarbamate, R_2NCSS^-; dtx^- = dithioxanthate, $ROCSS^-$; dtb^- = dithiobenzoate, $C_6H_5CSS^-$; dta^- = dithiophenylacetate, $C_6H_5CH_2CSS^-$. The dithiophosphate complex of iron(III) exhibits high-spin behavior while the *N,N*-diethyldithiocarbamate complex is an intermediate spin state, that is, exhibits a (high-spin)–(low-spin) equilibrium.[15,16] The other dithiolate ligands when complexed to iron(III) all induce low-spin states. Thus, the high-spin nature of the iron(III) complex of the cyclopentadienedithiocarboxylate ligand places the ligand with the dithiophosphate ligand in the spectrochemical series of dithiolate ligands.

The dinegative 1,1-dithiolate isomaleonitriledithiolate (imnt) has been reported to also form a tris high-spin iron(III) complex.[5] This ligand exhibits electronic properties similar to those for the $cdpt^{2-}$ system.[6] In fact, in all three of the ligands which are known to produce high-spin complexes ($cpdt^{2-}$, dtp^-, and $imnt^{2-}$) the negative charge is localized on the sulfur donor atoms. In the dtp^- case, the resonance form having a positively charged phosphorus and each sulfur negatively charged is expected to make a major contribution to the electronic structure of the ligand.[16] All of these ligands are better L → M π donors than the corresponding mononegative 1,1-dithiolates. Thus, the splittings between the d orbitals in dtp^-, $imnt^{2-}$, and $cpdt^{2-}$ are decreased relative to the other intermediates or low-spin dithiolate complexes.

Table IV. Electron Spin Resonance Parameters for $[(C_2H_5)_4N]_3Fe(C_5H_4CS_2)_3$

	g values
In CH_3CN (100 K)	9.30, 4.31, 0.77
Polycrystalline sample at room temperature	9.32, 4.15

The π-donor ability (presumable in-plane π donation) apparently overrides the σ-donor ability and the out-of-plane π-acceptor character of the $cpdt^{2-}$ ligand in the Fe(III) system. The proposed capability of the $cpdt^{2-}$ ligand to serve as a good π donor is substantiated by the large in-plane covalency exhibited by the cyclopentadienedithiocarboxylate in the molybdenyl(V) system.[18]

In order to understand further the electronic character of the iron(III) complex, an electron spin resonance study was undertaken. An obvious feature of the spectrum is an intense isotropic absorption at $g = 4.3$ observed both in the frozen solution and in a polycrystalline sample (Table IV). Some broadening of the spectrum is noted, apparently due to spin–spin interaction in the solid state.

A *g* value of 4.3 has been observed in other iron(III) systems which are of biological importance.[19-21] This is characteristic of a high-spin d^5 ($^6S_{5/2}$) state in which the zero-field splitting interaction is large. The Hamiltonian for a system which exhibits zero-field splitting may be written

$$\mathcal{H} = g\beta H\cdot S + S_z{}^2 - {}^1/_3S(S+1) + \lambda(S_x{}^2 - S_y{}^2)$$

Where $\lambda = 0$ corresponds to the situation of axial distortion and $\lambda = {}^1/_3$ corresponds to the situation of greatest rhombic distortion. Zero-field splitting gives rise to three Kramers doublets of the form

$$\psi_i^{\pm} = a_i|\pm{}^5/_2\rangle + b_i|\pm{}^1/_2\rangle + c_i|\pm{}^3/_2\rangle$$

Wickman et al.[19] have plotted g_{eff} vs. E/D (or λ) for the three doublets (D serves as a measure of the axial distortion). They observed for the iron(III) enzyme, ferrichrome A, a broad band of approximately 200 G at $g = 4.3$ for the transition of the middle doublet. They attributed the breadth of the peak to incomplete resolution of g_x, g_y, and g_z for a λ value less than ${}^1/_3$. A best fit was obtained for $\lambda = 0.25$.

Since our spectrum exhibits a narrower line of approximately 100 G, λ is tentatively assigned as ${}^1/_3$. Use of Wickman's plots dictates that the lower doublet transitions should occur at *g* equal to 9.6, 0.8, and 0.6. Closer inspections of both the polycrystalline and frozen-solution spectra show a broad peak at low field centered at about 9.3 and one other absorption at high field with a *g* value of 0.76. No other transitions were observed at temperatures as low as −160 °C.

For a g_{eff} value of 4.3, it is impossible to establish the sign of D as either positive or negative on the basis of the values of the **g** tensor for the lower doublet, since, for $\lambda = {}^1/_3$, the upper and lower doublets show transitions at the same positions. Furthermore, on the basis of the data presented here, it is impossible to separate the value of D from E.

In summary, the magnetic, Mössbauer and ESR parameters are all indicative of a high-spin, slightly distorted octahedral structure for the tris(cyclopentadienedithiocarboxylato)ferrate(III) ion. No evidence of any (high-spin)–(low-spin) interconversion is obtained.

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Registry No. $[(C_2H_5)_4N]_2Fe(C_5H_4CS_2)_2$, 57918-76-0; $[(C_2H_5)_4N]_3Fe(C_5H_4CS_2)_3$, 57918-78-2.

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Electron Paramagnetic Resonance of Chromium(III) Complexes of the Type *cis*-$[Cr(2,2'\text{-}bpy)_2XY]Z$, *cis*-$[Cr(1,10\text{-}phen)_2XY]Z$, and *cis*-$[Cr(ox)_2XY]Z$ in Frozen Solutions and Powders

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Frozen-solution spectra on X band as well as on Q band have been recorded for three series of Cr(III) complexes of the type *cis*-$[Cr(bpy)_2XY]Z$, *cis*-$[Cr(phen)_2XY]Z$, and *cis*-$[Cr(ox)_2XY]Z$, where XY is H_2O–H_2O, H_2O–OH^-, Cl^-–Cl^-, bpy, phen, ox, en, or acac. For some complexes the Cr-doped powder spectra of the corresponding Co(III) complexes have been recorded. The *D* values of the three series exhibited correlations with the ligand field strengths of the XY ligands. The rhombic distortions of the complexes varied from 0.05 to 0.33 D.

Introduction

This investigation was undertaken in order to provide data about the paramagnetic behavior of cis Cr(III) complexes and to correlate these data with parameters from the visible and ultraviolet spectra. Until now little work has been done on the EPR spectra[1] of cis complexes. On the other hand, various series of trans Cr(III) compounds[2–4] have been investigated. In the case of trans complexes it has become clear that for some series[3] the zero-field parameter *D* depends mainly on the difference of the ligand field strengths of the two substituting ligands on the one hand and the nonsubstituted ligands on the other hand. For other series[2,4] the correlations between *D* and the ligand field strengths are much less convincing. It is assumed that for the most part this is due to the position of the Z principal axis in the complex. In the first case this axis is situated perpendicular to the plane of the nonsubstituted ligands and in the latter case it lies in the plane. For cis Cr(III) complexes as studied in the present investigation, it can be expected that the behavior of the zero-field splitting *D* will reflect the cis substitution with respect to the ligand field strength, but to a smaller degree than in the case of purely tetragonal complexes because the Z axis is not situated in the plane of the XY ligands. Though these cis complexes are not strictly trigonal, they will be treated as such and in this paper will be described as trigonal in order to distinguish them from tetragonal complexes.[36]

Experimental Section

Preparation of Complexes. Most chromium and all cobalt complexes were prepared by established methods.[5–9] The complexes were characterized by means of ir spectroscopy.[9,37] The mixed complex with acetylacetonate, potassium acetylacetonatobis(oxalato)chromate(III) dihydrate, was prepared as follows. A 7.2-g sample of *cis*- or *trans*-$K_2[Cr(ox)_2H_2O(OH)]$[10] in 30 ml of 15% ethanol–water solution was boiled for 15 min with the stoichiometric amount of acetylacetone (2 ml). The green solution turned blue. With $BaCl_2$ in excess, $Ba[Cr(acac)(ox)_2]\cdot 2H_2O$ was precipitated. This compound was treated with the calculated amount of K_2SO_4 in about 10 ml of H_2O. To settle out the $BaSO_4$, the reaction mixture was allowed to stand for 0.5 h on a water bath. The filtrate was cooled to obtain blue-violet crystals of the K salt. Anal. Calcd for $C_9H_7O_{10}CrK_2$: C, 26.6; H, 1.7; O, 39.5. Found: C, 25.9; H, 1.7; O, 40.3.

EPR Spectra. All EPR spectra were recorded on a Varian Model 4052 spectrometer at approximately −160 °C on X band as well as on Q band. The magnetic field strengths were measured with an AEG gaussmeter. The frequency was determined with a Takeda Riken counter, Model 5502A, equipped with a No. 5023 frequency converter. The more soluble compounds were dissolved in a mixture of water, methanol, and dimethylformamide (WMD) of composition 1:8:1. Less soluble compounds were measured in a mixture of 3:4:3 composition by volume.[4]

The pH dependence of the aqua complexes was first established with aqueous solutions of various pH values, frozen in a Sephadex matrix[12] and then compared with the EPR spectra of a 6:2:2 WMD solution with the same pH. It appeared that there were only small differences between the two series, so for analyzing the data WMD frozen solutions were used. The EPR spectrum of *cis*-$[Cr(ox)_2H_2O(OH)]^{2-}$ was recorded in a buffered 6:2:2 WMD solution[34] at pH 8.6, while those of *cis*-$[Cr(bpy)_2H_2O(OH)]^{2+}$ and *cis*-$[Cr(phen)_2H_2O(OH)]^{2+}$ were both recorded[6] at pH 4.7.

The powders were prepared from aqueous solutions of the analogous Co(III) compounds to which 1–2% of the Cr complex was added. The solutions were allowed to crystallize in darkness in order to prevent decomposition.[9] For the measurements only well-shaped crystallites were used. As for $K[Cr(ox)_2phen]$, the analogous Co compound could not be prepared; this complex was added to the double complex[9] $[Co(ox)_2phen][Co(ox)(phen)_2]\cdot 3H_2O$. The EPR spectrum showed