

Table II. Bond Distances (Å) and Angles (deg), Standard Deviations in Parentheses

Te(1)-F(1)	1.849 (8)	Te(2)-F(4)	1.810 (5)
Te(1)-O	1.872 (5)	Te(2)-F(5)	1.819 (5)
Te(2)-F(2)	1.806 (5)	Te(2)-F(6)	1.806 (5)
Te(2)-F(3)	1.798 (6)	Te(2)-O	1.879 (5)
F(1)-Te(1)-F(1)'	180	F(3)-Te(2)-F(5)	90.9 (3)
F(1)-Te(1)-O	88.9 (2)	F(3)-Te(2)-F(6)	89.2 (3)
O-Te(1)-O'	90.0 (1)	F(3)-Te(2)-O	90.7 (3)
O-Te(1)-O''	177.9 (4)	F(4)-Te(2)-F(5)	88.9 (3)
F(2)-Te(2)-F(3)	90.0 (3)	F(4)-Te(2)-F(6)	89.7 (3)
F(2)-Te(2)-F(4)	90.2 (3)	F(4)-Te(2)-O	90.4 (3)
F(2)-Te(2)-F(5)	178.7 (3)	F(5)-Te(2)-F(6)	89.2 (3)
F(2)-Te(2)-F(6)	89.9 (3)	F(5)-Te(2)-O	93.8 (3)
F(2)-Te(2)-O	87.1 (2)	F(6)-Te(2)-O	177.0 (3)
F(3)-Te(2)-F(4)	178.9 (3)	Te(1)-O-Te(2)	139.4 (3)

molecule. The molecules are arranged in layers parallel to the *ab* plane with the F(1)-Te(1)-F(1)' axis perpendicular to the *ab* plane. The layer above (beneath) is shifted by 0.5*a* in the direction of the *a* axis (*b* axis), so that their centers lie in the hollows between the molecules of the first layer.

The molecules pack such that the ridges of adjacent molecules lie parallel. This arrangement gives good packing and explains why this is so far the only tellurium(VI) oxide fluoride solid at room temperature. The very recently synthesized *cis*-F₂Te(OTeF₅)₄ is in fact a liquid at room temperature.³ All intermolecular distances are longer than the sum of the van der Waals radii in question. The Te-F distances in the OTeF₅ group lie between 1.80 and 1.82 Å and are shorter than in the central octahedron Te(1)-F(1) = 1.85 Å. The similarity of the Te-F distances in the OTeF₅ group and their difference from the distance Te(1)-F(1) suggest that the different coordination of the two tellurium atoms has some unknown influence on the Te-F distances.

In U(OTeF₅)₆,⁷ the only other known structure with OTeF₅ groups, the temperature factors are very high and the distances are strongly affected by the thermal motion. The corrected values for the Te-F vary by ±0.06 Å and the mean value 1.86 (4) Å is somewhat greater than in this structure. Two structure determinations of gaseous TeF₆ give slightly different values: 1.86 (1)⁸ and 1.824 (4)⁹ Å. All known Te-F distances

for Te(VI) compounds lie in the range from 1.80 to 1.86 Å and are shorter than in Te(IV) compounds (1.86–2.01 Å)^{10–13}. The distances Te(1)-O and Te(2)-O are almost equal, but they are larger than in U(OTeF₅)₆,⁷ 1.81 Å (not corrected for thermal motion).

The angle of 139.4 (3)° at the oxygen atom deviates significantly from expected values like 109 or 120°. Similar values are found in some other Te-O compounds.¹⁴ A simple explanation for this effect is the repulsion between Te(1) and Te(2), which would otherwise come into too close contact.¹⁵ On the other hand in H₂Te₂O₃F₄¹³ the two tellurium atoms are also connected by an oxygen atom. The Te-O distance 1.919 (6) Å is only slightly greater, but the angle at the oxygen is some 20° smaller than in Te(OTeF₅)₄F₂. It can be assumed that in Te(OTeF₅)₄F₂ because of the high valency state of Te a considerable (p-d)_π bonding mechanism is the reason for this high angle value. This angle is only exceeded by the TeOTe angle in F₃Te-O-TeF₅ (145°), as was found recently by electron diffraction.¹⁶

Registry No. *trans*-F₂Te(OTeF₅)₄, 60788-81-0.

Supplementary Material Available: A listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of Pyrrole-*N*-carbodithioate Complexes of Selected Transition Elements¹

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Received April 17, 1977

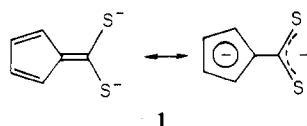
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The preparation and characterization of selected transition element complexes of the pyrrole-*N*-carbodithioate ligand (L) are reported. Specifically bis complexes with Cu(II), Cd(II), Pt(II), Pd(II), and Co(II) as well as a tris complex with Fe(III) have been isolated. A mixed chloride-ligand complex of Pt(IV), PtCl₂L₂, was also prepared. Infrared spectra of the metal complexes indicate an exocyclic single C-N bond, as opposed to other dithiocarbamate ligands. Computer analysis of the proton NMR spectra of the complexed and uncomplexed ligand indicates little positive charge buildup on the heterocyclic nitrogen atom, consistent with the infrared data. An electron spin resonance study of the Cu(II) complex yielded the following spin Hamiltonian parameters: $g_{\parallel} = 2.11$, $g_{\perp} = 2.02$, $A_{\parallel} = 144.8 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp} = 30.5 \times 10^{-4} \text{ cm}^{-1}$, $(g) = 2.07$, and $(a) = 62.2 \times 10^{-4} \text{ cm}^{-1}$. These data, when considered with the optical transition for this complex, are consistent with a very covalent σ and π metal-sulfur bond. These results when taken together illucidate the predominate electronic structure of the complexed ligand as being somewhat unique among dithiocarbamate systems.

Introduction

Since the first report by Cambi and co-workers over 35 years ago of the unusual properties of iron dithiocarbamate complexes,² a great deal of interest has centered on various examples of these ligand systems.^{3–6} Our interest in dithiocarbamate complexes arises from our extensive investigation

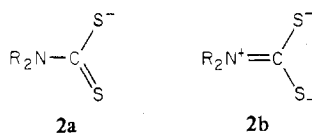
of the effects of resonance structures of the dianion of cyclopentadienedithiocarboxylic acid on the electronic structure of coordinated metals^{7–12} as depicted below. The results of this study clearly indicate that the driving force toward an aromatic five-membered ring creates a dominant π -accepting character at the sulfur atom and produces some unusual



1

properties at the coordinated metal center.

Traditionally, the interesting properties of dithiocarbamate complexes have been ascribed to a major contribution of a resonance structure in which a positive charge builds up on the nitrogen center, creating an effective dianion electronic structure.³



2a

2b

By the correct choice of R groups, a dithiocarbamate ligand can be constructed in which structure **2b** should not contribute to the overall electronic structure of the ligand system and potentially new and exciting metal complexes might result.

We chose to investigate this possibility by formally substituting a nitrogen atom for the bridgehead carbon in our original dithiolate system which results in a pyrrole-*N*-carbodithioate. Obviously, a structure in which a positive charge buildup on the nitrogen occurs results in a nonaromatic five-membered ring system and should not be important. Kellner et al.¹³ offer a brief report on an infrared study of several transition element complexes of this ligand system. Yet based on our previous work, a more detailed and systematic study seems warranted.

Experimental Section

Materials. Reagent grade tetrahydrofuran and hexanes were dried over Na/K alloy and benzophenone. Acetonitrile was dried by repeated distillation from phosphorus pentoxide. Chloroform and pyridine were dried over Davison 4 Å molecular sieves. CuCl₂, FeCl₃, CoCl₂, CdBr₂, PdCl₂, PtCl₂, and PtCl₄ were obtained from Research Organic/Inorganic, Inc., and used without further purification.

Preparation of Compounds. C₄H₄NCS₂·K·C₄H₈O. To 100 mL of tetrahydrofuran was added 2 g (2.1 mL, 0.03 mol) of pyrrole and 1.165 g (0.03 mol) of metallic potassium. The resulting white precipitate was filtered, washed with three 20-mL portions of tetrahydrofuran, dried in vacuo, and transferred to a flask containing 50 mL of tetrahydrofuran at -78 °C. With continuous stirring, 2.26 g (1.8 mL, 0.03 mol) of CS₂ was added dropwise over a 0.5-h period. The resulting red-yellow solution was stirred for an additional 1.0 h. After this period of time, chilled, degassed hexanes were added to the point of incipient precipitation. The solution was refrigerated for 12.0 h after which time bright yellow needles of the complex form (% yield >95%, mp 143–145 °C). Anal. Calcd for KC₃H₄NCS₂·C₄H₈O: C, 42.66; H, 4.77; N, 5.53; S, 25.30. Found: C, 42.30; H, 4.30; N, 5.48; S, 25.30.

(C₄H₄NCS₂)₂Cu. To 100 mL of tetrahydrofuran at -78 °C was added 0.195 g (1.5 × 10⁻³ mol) of CuCl₂ and 0.7351 g (3.0 × 10⁻³ mol) of the potassium salt of the ligand. The mixture was stirred for 5 h during which time the temperature was allowed to reach 0 °C. The resulting red-brown solution was filtered, reduced to one-half its original volume, and refrigerated. A fine brown precipitate of the complex was finally collected (mp >290 °C). Anal. Calcd for C₁₀H₈N₂S₄Cu: C, 34.50; H, 2.34; N, 8.05. Found: C, 34.34; H, 2.42; N, 7.93.

In general, other metal complexes resulted from a similar procedure as that employed for the Cu(II) complex. In all cases except the copper preparation, crystalline products were obtained. Acceptable elemental analyses were found for all compounds (similar to the Cu(II) product) and tables of these data are available in the microfilm addition of this journal.

(C₄H₄NCS₂)₂Cd. This bright yellow complex resulted from typical starting materials of 0.680 g (2.4 × 10⁻³ mol) of CdBr₂ and 1.20 g (4.7 × 10⁻³ mol) of the potassium salt of the ligand (mp >290 °C).

(C₄H₄NCS₂)₂Pd. This bright orange complex resulted from typical starting materials of 0.200 g (1.12 × 10⁻³ mol) of PdCl₂ and 0.5716

g (2.25 × 10⁻³ mol) of the potassium salt of the ligand (mp >290 °C).

(C₄H₄NCS₂)₂Pt. This bright red complex resulted from typical starting materials of 0.200 g (7.5 × 10⁻⁴ mol) of PtCl₂ and 0.386 g (1.5 × 10⁻³ mol) of the potassium salt of the ligand (mp >280 °C).

(C₄H₄NCS₂)₃Fe·1/2C₄H₈O. This dark red complex resulted from typical starting materials of 0.25 g (1.5 × 10⁻³ mol) of FeCl₃ and 1.15 g (4.5 × 10⁻³ mol) of the potassium salt of the ligand. The first fraction of product obtained upon refrigeration of the reaction mixture was discarded since it contained a great deal of KCl. The volume of the mixture was again reduced and dark red crystals resulted (mp 196 °C).

(C₄H₄NCS₂)₂Co·1/2C₄H₈O. This green complex resulted from typical starting materials of 0.300 g (2.3 × 10⁻³ mol) of CoCl₂ and 1.17 g (4.6 × 10⁻³ mol) of the potassium salt of the ligand (mp >220 °C).

(C₄H₄NCS₂)₂PtCl₂·1/2C₄H₈O. This bright orange complex resulted from typical starting materials of 0.200 g (5.9 × 10⁻⁴ mol) of PtCl₄ and 0.602 g (2.3 × 10⁻³ mol) of the potassium salt of the ligand.

(C₄H₄NCS₂)₂Cd(Cu) or (C₄H₄NCS₂)₂Pd(Cu). Samples of Cu(C₄H₄NCS₂)₂ doped into the corresponding cadmium (or palladium) matrix in a 500:1 ratio were obtained by simply preparing the cadmium complex in the presence of a copper impurity. The reactions were carried out in tetrahydrofuran as described above except that the doped complex was immediately precipitated with hexane after the initial filtration. This is required because of the different solubilities of the two compounds.

Analyses. Analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn., and the Charles C. Kavin Co., Buffalo, N.Y.

Methods. All reactions were carried out under an argon atmosphere using Schlenk techniques. ESR, NMR, and UV-visible samples were prepared in glovebags. NMR and melting point tubes were sealed under vacuum in the case of potassium pyrrole-*N*-carbodithioate.

Spectroscopic Measurements. Infrared spectra were obtained as Nujol mulls and KBr pellets on a Perkin-Elmer Model 467 spectrophotometer. Optical spectra were obtained as mulls in Nujol (diffuse absorption), in CHCl₃ and CH₃CN on a Cary Model 14 spectrophotometer. Electron spin resonance spectra were obtained at 9.0 GHz employing a Varian E-9 spectrometer coupled to a Hewlett Packard frequency meter and DPPH as a *g*-value standard. All ESR spectra were obtained at 100 K under conditions previously described.⁷⁻⁹ Nuclear magnetic resonance spectra were obtained employing a Varian XL-100 Fourier transform spectrometer. Spectra obtained are the results of 50 computer averages.

Computer Simulation of NMR Spectra. Computer simulation of the proton NMR spectra for the ring protons on the pyrrole-*N*-carbodithioate ligand as a potassium salt and when complexed to cadmium was accomplished through use of a program written by Bothner-By and Castellano¹⁴ and kindly supplied by Professor H. L. Ammon of the University of Maryland.

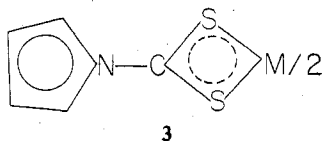
Frequencies for the A and B protons (A₂B₂ system) were assigned according to data from the average spectra. On the basis of other work on substituted pyrrole systems, coupling constants were established to yield a spectrum which resembled the experimental one. The output generated consisted of possible transitions along with estimated intensities. Using the computer generated spectrum which most closely resembled the experimental one, line assignments were made. Then an iterative procedure was followed to match the calculated and experimental line positions. On this basis, tables of chemical shifts, coupling constants, and calculated line frequencies (and intensities), as well as an error analysis, were generated.

Results and Discussion

The pyrrole-*N*-carbodithioate anion is an interesting ligand for several reasons. First, an early report by Duffy et al.¹⁵ indicated that this particular dithiocarbamate could not be prepared, because of the low basicity of the amine hydrogen. In addition, the first report by Kellner et al. of the synthesis of this dithiocarbamate expressed some concern that a rearrangement might occur to yield the 2-substituted pyrrole anion. Second, this ligand system should not allow for the normal resonance structures ascribed to dithiocarbamates where a positive charge can build upon the nitrogen atoms. Thus, a potentially new set of properties of the metal complexes might occur.

Potassium pyrrole-*N*-carbodithioate (pdtc) is a bright yellow air-sensitive solid. The absence of an N-H infrared band coupled with a clear A_2B_2 proton NMR spectrum and no N-H proton peak clearly identifies the salt as the nitrogen-substituted molecule. Interestingly the metal complexes are quite air stable, decomposing only slowly upon exposure to the air. In nonaqueous solvents, decomposition is more rapid upon exposure to the atmosphere, yielding metal sulfides after 8–10 h.

The relevant features of the infrared and optical spectra of K^+pdtc^- and the metal complexes as well as suggested assignments are available in the microfilm addition of this journal. The strong absorption in the infrared spectra of the metal complexes in the 1250–1350 cm^{-1} region (C–N single bond)^{16,17,18} suggests a predominance of resonance structure, **2a**. Unlike the previously studied cyclopentadienedithiocarboxylate dianion (1) where the predominate resonance structure results from a driving force toward an aromatic structure, the predominate resonance structure of the pyrrole-*N*-carbodithioate monoanion results from a tendency to not disturb the aromaticity of the pyrrol ring. Yet it is also entirely possible that this ligand may have bonding characteristics similar to other dithiocarbamates since it has been suggested that the extensive π delocalization in other dithiocarbamate ligands involved *only* the metal and CS_2 group:

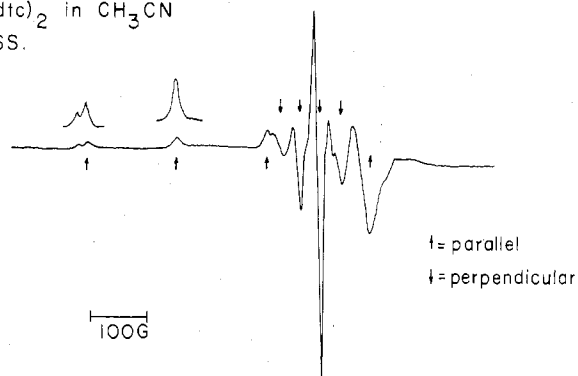


Fortunately, the electronic structure of this particular dithiocarbamate can be systematically characterized. Electron spin resonance (ESR) studies of paramagnetic complexes, i.e., Cu(II) or Co(II), have been employed to determine the extent of covalent σ and π bonding between metal and ligand. Furthermore, nuclear magnetic resonance (NMR) characterization of the ring protons can be used to characterize the electronic structure of the remaining portion of the ligand. Thus, an overall electronic and structural picture can be developed.

Either the Cu(II) (d^9) or Co(II) (d^7 low spin) complexes could be informative in establishing the *relative* bonding structure of the metal–sulfur system. The Co(II) system did not yield a well-resolved ESR spectrum as before.⁸ The bis(pyrrole-*N*-carbodithioate)copper(II) complex in its pure form exhibits an ESR spectrum typical of a dimeric species involving metal–metal interaction. However, in frozen solutions and in dilute matrices (Cd/Cu or Pd/Cu = 500/1) well-resolved parallel and perpendicular components indicative of a local D_{4h} or lower symmetry is observed (Figure 1). Even in the dilute matrices, weak features of the dimeric species are still observed. This triplet character has been observed for bis(diethylthiocarbamate)copper(II) as well.^{19–21} Since the spin Hamiltonian parameters are virtually identical for the predominate species in frozen CH_3CN (100 K) and the corresponding Cu(II) or Pd(II) matrix, there is little doubt that this species is a four-coordinate copper(II) species. A five-coordinate complex in the Cd or Pd matrix could require a five-coordination (and a dimer ESR) in frozen solution which can be observed but does not correspond to the dilute matrix data. The parameters for the Cu(II) monomer are $A_{||} = 144.8 \times 10^{-4}$, $A_{\perp} = 30.5 \times 10^{-4} cm^{-1}$, $g_{||} = 2.11$, and $g_{\perp} = 2.02$. The isotropic solution spectrum in CH_3CN (ambient room temperature) yielded $\langle a \rangle = 62.2 \times 10^{-4} cm^{-1}$ and $\langle g \rangle = 2.07$.

Based on the observation that only parallel and perpendicular components are observed in the ESR spectrum, we can assume that the effective local symmetry at the copper center involves a C_4 symmetry element. In these cases, the forms for

ESR SPECTRUM OF
Cu(pdtc)₂ in CH₃CN
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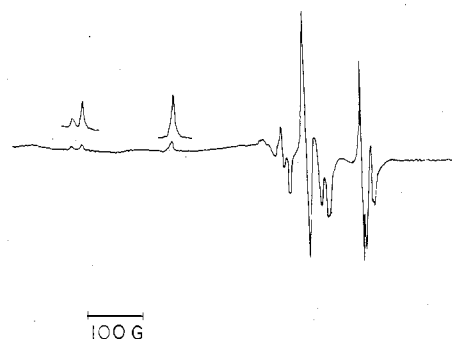


Figure 1. (Top) Spectrum of $Cu(C_4H_5NCS_2)_2$ in CH_3CN . (Bottom) Spectrum of $Cu(C_4H_4NCS_2)_2$ in doped matrix (Cd/Cu = 500/1).

the molecular orbitals involving metal d and sulfur orbitals take the well-established form^{22,23}

$$\psi_{B1g} = \alpha d_{x^2-y^2} - 1/2\alpha' [-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)}] \quad (1)$$

$$\psi_{B2g} = \beta d_{xy} - 1/2(1 - \beta^2)^{1/2} [P_y^{(1)} + P_x^{(2)} - P_y^{(3)} - P_x^{(4)}] \quad (2)$$

$$\psi_{A1g} = \gamma d_{z^2} - 1/2(1 - \gamma^2)^{1/2} [\sigma_x^{(1)} + \sigma_y^{(2)} - \sigma_x^{(3)} - \sigma_y^{(4)}] \quad (3)$$

$$\begin{aligned} \psi_{Eg} &= \delta d_{xz} - (1 - \delta^2)^{1/2} [P_z^{(1)} - P_z^{(3)}] / 2^{1/2} \\ &= \delta d_{yz} - (1 - \delta^2)^{1/2} [P_z^{(2)} - P_z^{(4)}] / 2^{1/2} \end{aligned} \quad (4)$$

Overlap is included only for the ψ_{B1g} state where α and α' are related by²³

$$\alpha^2 + \alpha'^2 - 2\alpha\alpha'S = 1 \quad (5)$$

where S is the metal–ligand overlap term (0.005) and the σ orbitals are hybridized sp orbitals. Using a slightly modified set of equations from those developed first by Kivelson and Nieman²⁴ along with the observable ESR parameters, α , β , and δ can be determined from the following equations⁷

$$g_{||} = 2.0023 - (8\lambda/\Delta E_{xy})\alpha^2\beta^2 \quad (6)$$

$$g_{\perp} = 2.0023 - (2\lambda/\Delta E_{xz})\alpha^2\delta^2 \quad (7)$$

$$A_{||} = P\alpha^2 \left\{ -(4/7 + k) - 2\lambda \left[\frac{4\beta^2}{\Delta E_{xy}} + \frac{3}{7} \frac{\delta^2}{\Delta E_{xz}} \right] \right\} \quad (8)$$

λ is the spin–orbit coupling constant for the free ion and is taken as $-828 cm^{-1}$ and k corrects for the Fermi contact term of excited configurations of copper and was taken as $3/7$.²⁴ P was taken as $0.036 cm^{-1}$. The ΔE_{xy} transition for the copper(II) complex can confidently be assigned a value of $1.89 \mu m^{-1}$. In addition, a band at approximately $2.24 \mu m^{-1}$ can be ruled out as a possible ΔE_{xz} transition since it also appears

Table I. Bonding Parameters for $\text{CuL}_2^{(0,2-)}$ Systems

Ligand	α	β	δ	α'
Diethyldithiocarbamate	0.73	0.72	0.92	0.69
Cyclopentadienedithiocarboxylate	0.77	0.70	0.72	0.64
Pyrrole- <i>N</i> -carbodithioate	0.72	0.76	0.77	0.70

in the spectra of the dimeric species. Although solubility did not allow any accurate calculation of the extinction coefficient, dilution of the copper solutions did cause a dramatic decrease in the intensity of this band. Since it is obvious that dilution results in a decrease of intensity for spectral bands, the fact that a 1:1 correspondence in the "approximate" values calculated for the extinctions did not conform suggests that this band is entirely due to the presence of small amounts of dimer which was shown to be present in the ESR spectrum.

This leaves either a band at 2.75 or $2.84 \mu\text{m}^{-1}$ as an appropriate choice for ΔE_{xz} . It is quite possible that these absorptions do not arise from d-d transition but rather from ligand to metal charge-transfer absorption. Nevertheless, their use as an upper limit to this transition will introduce only small errors in the values for β and δ .²⁵ Of the two, the band at $2.84 \mu\text{m}^{-1}$ might be eliminated, since a band close in energy is also found for the cadmium complex ($2.89 \mu\text{m}^{-1}$). These bands must be attributed then to metal to ligand charge transfer. Since no other absorptions are present below $2.89 \mu\text{m}^{-1}$ in the cadmium complex, the band at $2.75 \mu\text{m}^{-1}$ is the most likely choice for the ΔE_{xz} transition.

Substituting these values and solving eq 6-8 lead to the following parameters: $\alpha = 0.72$, $\beta = 0.76$, $\delta = 0.77$, $A_{\perp \text{calcd}} = 21.6 \times 10^{-4} \text{ cm}^{-1}$, and $A_{\perp \text{obsd}} = 30.5 \times 10^{-4} \text{ cm}^{-1}$.

The values obtained indicate strong covalency in the in-plane σ bonding and moderate covalency in the in-plane and out-of-plane π bonding. This strong in-plane bonding can be attributed to the ability of sulfur atoms to form covalent bonds and thus delocalize the metal d electrons.^{19,26} Similar results were also obtained for copper diethyldithiocarbamate^{19,20} and copper cyclopentadienedithiocarboxylate⁷ studied earlier.

Of particular interest is the relative importance of the out-of-plane π bonding. Table I compares the appropriate parameters for these three systems.

Although the value of δ for this system is indicative of a situation which is not as highly covalent as in the cyclopentadienedithiocarboxylate case, it does nevertheless demonstrate that this ligand acts as a moderate π -bonding ligand when compared to either of the CuL_2 systems in Table I. Since this out-of-plane π bond is antibonding in character and is moderately covalent, the bonding molecular orbital should be similar, implying that this dithiocarbamate might be capable of limited π bonding. It may very well be that this π bonding is localized in the metal chelate ring, rather than being delocalized throughout the entire molecule as observed before^{7,12} to give the overall bonding situation depicted above (3).

NMR Study

The proton NMR spectrum of any diamagnetic complex potentially could be used to determine the electronic structure of the pyrrole portion of this ligand. We previously have characterized the Zn(II) and Cd(II) complexes of the cyclopentadienedithiocarboxylate ligand in this manner.¹⁰ In this case, the Cd(II) complex was investigated as well as the potassium salt.

The pyrrole ring portion of both systems shows an NMR characteristic of a complex A_2B_2 system, where the complex multiplets for the ligand and its cadmium complex are centered at 8 and 6 ppm and 7.7 and 6.3 ppm, respectively. Values for the coupling constants were obtained by use of a computer program written by Castellano and Bothner-By as described above. In each case, estimates of "reasonable" J values on the basis of other work on pyrrole systems were used as a

Table II

	Pyrrole	Pyrrole- <i>N</i> -carbodithioate	Cadmium pyrrole- <i>N</i> -carbodithioate
J_{12} , Hz	2.70	2.58	2.44
J_{13} , Hz	1.44	2.21	2.12
J_{14} , Hz	1.88	2.75	2.82
J_{23} , Hz	3.35	2.71	2.64
J_{24} , Hz	1.44	2.21	2.12
J_{34} , Hz	2.70	2.58	2.44

Table III

	p_{1-2}	p_{2-3}
Pyrrole	0.54	0.63
Pyrrole- <i>N</i> -carbodithioate	0.53	0.55
Cadmium pyrrole- <i>N</i> -carbodithioate	0.51	0.54

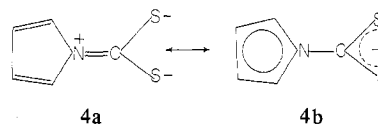
starting point to generate a workable system. For the system under investigation, the coupling constants for pyrrole proved to be the most efficient. Experimentally determined transitions were matched with calculated ones to achieve a best fit according to a least-squares criterion. For pyrrole-*N*-carbodithioate the maximum error was 0.177 Hz while that for the cadmium complex was 0.176 Hz. However, most of the other transitions show much better agreement with the observed transitions with a maximum error of <0.09 Hz.

Using the data from Smith et al.²⁷ the 1-2 and 2-3 carbon bond orders (see Table II) can be determined based on the coupling constants which are listed in Table III. According to the criterion of Streitwieser²⁸ $p > 0.80$ corresponds to a double bond, $p < 0.4$ corresponds to a single bond, and $p = 0.5-0.7$ corresponds to a bond in an aromatic system. It is apparent from the data in Table II that the aromatic character in going from pyrrole to the carbodithioate to finally the cadmium species is essentially unchanged.

This is quite novel if one realizes the fact that in virtually all other dithiocarbamate complexes, resonance in **2b** plays a paramount role in these transition metal analogues.

However, apparently the pyrrole-*N*-carbodithioate analogue is the first dithiocarbamate complex to exhibit only the mononegative form **4b**

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when complexed to transition metals. It is apparent then that not only is the conjugated diene structure eliminated in metal analogues of this dithiocarbamate but also the extensive π system observed in other analogues such as cyclopentadienedithiocarboxylate is also absent.

As a final investigation into this system, we are examining the anomalous spin-crossover behavior of the Fe(III) analogue. Tentatively, it appears that the majority of bands in the UV-visible spectrum are assignable to the low spin state. Assuming that this increased covalency as observed above resulted in a shortening of the M-S bond (3), one would then naturally expect that the ligand field splitting parameter, Δ , would also increase. This would favor the low spin state and resonance form **4b**. The optical spectrum of the Fe(III) complex is complex. Although the predominate bands could be confidently assigned to a Fe(III) low-spin system, weaker features exist which might be assigned to either a low-spin or high-spin system.²⁹ Similar discussions of this phenomena have been presented by Duffy et al.¹⁵ who in fact proposed that five-member rings such as pyrrole, indole, carbozole, imidazole,

succinimide, and indoline should in fact favor the low-spin state.³⁰ This corresponds to form **4b** which we have proposed. Unfortunately, to date only the indoline derivative has been reported³¹ and it was shown by Mössbauer isomer shift to be low spin.

Acknowledgment. We would like to thank Professor D. Chasteen of the University of New Hampshire for allowing us use of the Q-band ESR spectrometer and also Professor H. L. Ammon of the University of Maryland for use of computer programs used in the NMR spectral analysis. R.D.B. gratefully acknowledges a Camille and Henry Dreyfus Foundation Fellowship.

Registry No. K(pdte), 62641-74-1; Pd(pdte)₂, 63765-42-4; Pt(pdte)₂, 63765-41-3; Cd(pdte)₂, 52676-51-4; Fe(pdte)₃, 63765-40-2; Co(pdte)₂, 63765-39-9; Cu(pdte)₂, 61155-98-4; PtCl₂(pdte)₂, 63765-38-8; pyrrole, 109-97-7; CS₂, 75-15-0.

Supplementary Material Available: Tables of analytical results and IR and UV-visible data (4 pages). Ordering information is given on any current masthead page.

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Transition Metal Ions in High Formal Oxidation States. Synthesis and Structural Characterization of the Six-Coordinate Iron(IV) Complex of the 1,1-Dicarboethoxy-2,2-ethylenedithiolate Chelating Ligand

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Received March 25, 1977

AIC702213

The synthesis and structural characterization of bis(benzyltriphenylphosphonium) tris(1,1-dicarboethoxyethylene-2,2-dithiolato)ferrate(IV), [C₇H₇(C₆H₅)₃P]₂[(S₂CC(COOC₂H₅)₂)₃Fe] (I), are described. Complex I crystallizes in the monoclinic space group C2/c with four molecules per unit cell. The cell dimensions are $a = 19.114$ (6) Å, $b = 15.424$ (5) Å, $c = 24.308$ (8) Å, and $\beta = 97.50$ (2)°. Intensity data were collected with a four-circle computer-controlled diffractometer using the $\theta-2\theta$ scan technique. All of the atoms in the complex anion and the phosphorus atom in the cation were refined anisotropically. The carbon atoms in the cation were refined isotropically. The hydrogen atoms were included in their predicted positions but were not refined. Refinement by full-matrix least squares on 2350 data for 305 parameters gave a final R value of 0.042. The geometry of the MS₆ moiety in the structure can be described as originating from a trigonal prism which suffers individual rotations of the chelating ligands around the C₂ axes. One of these rotations is more severe than the other two causing a lowering of the overall symmetry to C₂. Values of selected bond distances and bond angles are as follows: Fe-S, 2.289 (2), 2.305 (2), and 2.301 (2) Å; S-S (intraligand), 2.737 (3), and 2.786 (2) Å; S-Fe-S (trans), 159.52 (8) and 158.75 (5)°; S-Fe-S (bite), 74.66 (6) and 72.97 (5)°. A description of the bonding is presented that attributes the stability of the complex to Fe(IV)-S bonding with considerable covalent character.

Introduction

The stability of complexes with metal ions in unusually high formal oxidation states depends to a great extent on the σ -bonding and π -back-bonding properties of the ligands. With sulfur ligands, the ability of the sulfur atoms to participate in π bonding in addition to σ donation allows for the formation of oxidized complexes in which the oxidation state of the metal ion, at least formally, can be described as unusually high. The concept of the "formal" oxidation-state description for the metal ions in oxidized sulfur chelate complexes is an attempt to by-pass the ambiguity concerning the site of oxidation in these complexes, since very often the possibility of ligand

centered oxidations or interligand oxidative interactions does not allow for an unambiguous description of the nature of the oxidation.

Among the 1,1-dithio chelates, the dithiocarbamate ligand seems to stabilize high formal oxidation states of transition metal ions in a variety of complexes.² The ambiguity described previously also is applicable to oxidized dithiocarbamate complexes where interligand oxidative interactions possibly could account for the stability of the oxidized chelates.³ A description which is more in agreement with experimental facts, however, is one that attributes the stability of highly oxidized metal ions in dithiocarbamate complexes to a π -