

The hydrated compound pelleted in KCl gives a spectrum like that obtained for the KI pelleting; however, the anhydrous compound in KCl yields a spectrum where the low-field signal at 2.178 is quite weak and the high-field feature at 2.063 is shouldered with a signal at ~ 2.084 .

All in all, it looks like hydration and dehydration are the major occurrences with pelleting of these two oxalatocopper perchlorates. The pelleted species, however, do not seem to have exactly the same copper environments as are found in the hydrated or anhydrous material and as such additional work is needed to eliminate the possibility of anation, partial dissociation of oxalate, etc. This becomes more than amply clear when one views the Q-band spectrum (see Figure 12, tracing C) of a sample of $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$ pelleted in KBr. This spectrum seems to be a superposition of spectral features from at least two different copper species.

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Registry No. $\text{Cu}(\text{dien})(\text{Ox})\cdot 4\text{H}_2\text{O}$, 37072-95-0; $[\text{Cu}_2(\text{dien})_2(\text{Ox})(\text{ClO}_4)_2]$, 50797-94-9; $[\text{Cu}_2(\text{dien})_2(\text{Ox})(\text{ClO}_4)_2\cdot\text{H}_2\text{O}]$, 55401-14-4; $[\text{Cu}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$, 40961-76-0; $[\text{Zn}_2(\text{dien})_2(\text{Ox})](\text{BPh}_4)_2$, 55520-75-7; $[\text{Cu}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$, 55401-16-6; $[\text{Zn}_2(\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$, 55520-76-8; $[\text{Cu}_2(\text{dien})_2(\text{NCO})_2](\text{BPh}_4)_2\cdot 2\text{H}_2\text{O}$, 55401-19-9; $[\text{Zn}_2(\text{dien})_2(\text{NCO})_2](\text{BPh}_4)_2$, 55520-74-6; $\text{Cu}(\text{dien})(\text{NCS})_2$, 52690-20-7; $[\text{Cu}_2(\text{dien})_2(\text{NCS})_2](\text{ClO}_4)_2$, 52588-10-0; $[\text{Cu}_2(\text{dien})_2(\text{NCS})_2](\text{BPh}_4)_2$, 55401-20-2.

Supplementary Material Available. Tables I and II, showing analytical results and $[\text{Cu}_2(\text{dien})_2(\text{C}_2\text{O}_4)](\text{BPh}_4)_2$ magnetic susceptibility data, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105×148 mm, $24\times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC40832K.

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Complexes with Sulfur and Selenium Donors. XI. Metal 2-Amino-1-cyclopentene-1-dithiocarboxylates^{1,2}

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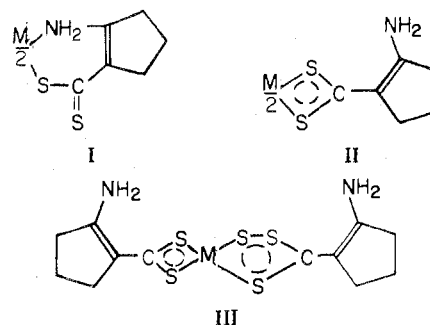
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A variety of complexes of the 2-amino-1-cyclopentene-1-dithiocarboxylate (acdc) anion have been investigated with a view to elucidation of the bonding sites employed by the acdc ligand. Electron spin resonance spectra of $\text{VO}(\text{acdc})_2$ and $\text{Cu}(\text{acdc})_2$ and proton NMR spectra of $\text{Zn}(\text{acdc})_2$, $\text{Cd}(\text{acdc})_2$, $\text{Hg}(\text{acdc})_2$, $\text{Ni}(\text{acdc})_2$, and $\text{In}(\text{acdc})_3$ as well as the electronic spectra of the complexes support the exclusive use of sulfur atoms by the ligand in metal bonding.

Introduction

Metal complexes with sulfur donor ligands exhibit a wide variety of chemical behavior. The physical and chemical properties of these compounds have been extensively reviewed.³⁻⁶ A series of complexes of the type ML_2 (M = divalent Ni, Co, Pt, Zn, and Cd; L = the 2-amino-1-cyclopentene-1-dithiocarboxylate (acdc) anion) were investigated by Pattnaik and Sen.⁷ They suggested that these complexes contained MS_2N_2 chromophores (I). In view of previous work with sulfur donor ligands we considered the formation of quadratic MS_4 chromophores (II) a more likely possibility and, thus, undertook the present study. A referee kindly pointed out the work of Thomas and Poveda,⁸ who investigated acdc complexes with divalent Co, Ni, Cu, Zn, and Cd ions. They proposed⁸ on the basis of rather limited measurements of

physical properties that MS_4 chromophores were obtained and that Co(II) and Ni(II) formed complexes of type III. Pattnaik



and Sen's suggestion⁷ of involvement of the amino group in

Table I. Analytical Data for Metal 2-Amino-1-cyclopentene-1-dithiocarboxylates^a

Compd	Color	Calcd			Found		
		% C	% H	% N	% C	% H	% N
Ni(acdc) ₂	Purple	38.40	4.27	7.48	38.68	4.42	7.33
Cu(acdc) ₂	Brown	37.92	4.21	7.37	37.49	4.13	7.19
VO(acdc) ₂	Green	37.58	4.16	7.31	35.58	3.78	6.24
Zn(acdc) ₂	Yellow	37.74	4.22	7.34	37.59	4.18	7.35
Cd(acdc) ₂	Yellow	33.66	3.76	6.53	33.81	3.86	6.65
Hg(acdc) ₂	Yellow	27.87	3.12	5.42	27.60	3.28	5.69
Int(acdc) ₃	Yellow	36.67	4.10	7.13	35.02	4.09	6.72

^a The purity of NH₄acdc itself was monitored by checking its quantitative reaction with aqueous nickel(II) chloride. In a typical experiment 0.1577 g of NH₄acdc yielded 0.1727 g of Ni(acdc)₂ (0.1714 g calculated).

metal binding was entirely based on infrared spectral studies in which they observed shifts of the amino group stretching frequencies to lower wave numbers upon complex formation.

Such amino group shifts might also be associated with changes in the delocalization of the amino nitrogen lone-pair electrons or intramolecular or intermolecular interactions not involving metal coordination. We have conducted electron spin resonance (ESR), proton nuclear magnetic resonance (PMR), and further infrared spectral studies of acdc complexes in order to elucidate further the mode of metal-ligand bonding. Furthermore, new complexes of mercury, vanadyl, and indium ions have been prepared and characterized. The VO(acdc)₂ complex was found to be unstable as might be expected from data available for vanadyl dithiocarbamates.⁹ However, the copper(II) bis(chelate) complex was surprisingly stable.

Experimental Section

All chemicals were of the best available reagent or spectroscopic grade. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., and Chemalytics, Inc., Tempe, Ariz.

Ammonium 2-amino-1-cyclopentene-1-dithiocarboxylate, NH₄(acdc), was prepared by the method described previously¹⁰ and was recrystallized from absolute ethanol. The metal complexes were obtained by adding a stoichiometric amount of metal salt (chloride, nitrate, or sulfate) to an aqueous solution of the ligand. The complexes, which precipitated immediately, were isolated by filtration and washed with warm water followed by absolute ethanol. Since the compounds were not soluble in common solvents, they were not recrystallized. The complexes were dried in a vacuum desiccator over anhydrous calcium chloride. Elemental analyses (Table I) indicate that the vanadyl complex is unstable—this is discussed further in the text. Polycrystalline samples of VO(acdc)₂ and Cu(acdc)₂ doped into the nickel(II) complex were prepared as were the pure compounds by adding an appropriate mole percent mixture of the metal salts to a solution of the ligand.

Infrared spectra (4000–200 cm⁻¹) were obtained using Nujol mulls on cesium iodide plates and potassium bromide pellets with a Perkin-Elmer Model 621 recording spectrophotometer. Spectra were calibrated with polystyrene film. Electronic spectra were obtained with a Cary Model 14 recording spectrophotometer and matched 1.0-cm quartz cells. Mull (transmittance) spectra were obtained by a technique described previously.¹¹ Proton nuclear magnetic resonance spectra were obtained with a Varian T-60 spectrometer operating at 35°. Tetramethylsilane (TMS) was employed as an internal standard. Electron spin resonance spectra were recorded with a Varian EM-500 spectrometer at room temperature. Spectra were calibrated using diphenylpicrylhydrazyl (DPPH) as a field marker and a solution of oxobis(2,4-pentanedionato)vanadium(IV) in benzene as a field marker and field sweep monitor. The utility of this double standard calibration technique was confirmed with other ESR equipment described earlier.¹² Quartz sample tubes were employed for polycrystalline samples and capillary tubing was used for solution samples.

Results and Discussion

ESR Spectra. The ESR spectra of VO(acdc)₂ and Cu(acdc)₂ doped into the corresponding diamagnetic nickel(II)

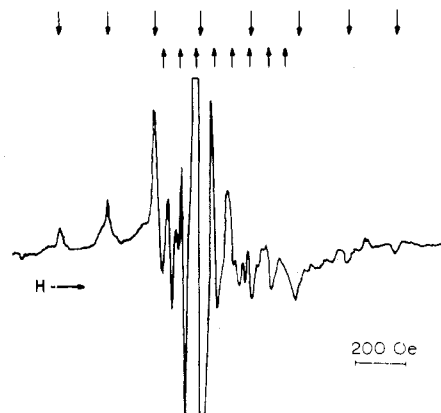


Figure 1. ESR spectrum of VO(acdc)₂ doped into the corresponding diamagnetic nickel(II) complex. The arrows pointing downward indicate the parallel absorptions while those pointing upward indicate the perpendicular resonant field positions.

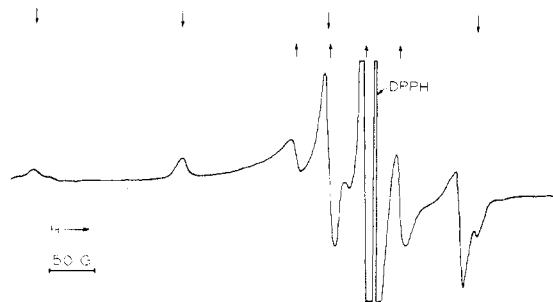


Figure 2. ESR spectrum of Cu(acdc)₂ doped into the corresponding diamagnetic nickel(II) complex. The arrows pointing downward indicate the parallel absorptions while those pointing upward indicate the perpendicular resonant field positions.

complex are shown in Figures 1 and 2, respectively. The solution ESR spectra of VO(acdc)₂ and Cu(acdc)₂ exhibited the expected eight- and four-line patterns, respectively. Since the ligand yields a diamagnetic nickel(II) complex, nitrogen superhyperfine splitting in the ESR spectrum of the doped Cu(II) complex might be anticipated if the amino group is involved in metal binding. However, no nitrogen superhyperfine splitting was observed in the ESR spectrum. This, in itself, is not conclusive of no Cu–N bonding. It was also noted that the Cu(acdc)₂ complex exhibited narrow line widths characteristic of CuS₄ compounds. The axial spin Hamiltonian

$$\hat{H} = g_{\parallel}\beta H_z \hat{S}_z + g_{\perp}\beta(H_x \hat{S}_x + H_y \hat{S}_y) + A_{\parallel}\hat{I}_z \hat{S}_z + A_{\perp}(\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y) \quad (1)$$

where the symbols have their usual meanings, was employed in the analysis of anisotropic spectra of both the VO(acdc)₂ (d¹ system) and Cu(acdc)₂ (d⁹ system) complexes. Stick diagrams correct to second-order were calculated and matched to the observed spectra.¹³ In the absence of crystal structure data for the complexes, single-crystal studies were not attempted and it was assumed that the *g* and *A* tensors share the same principal-axis system. Table II collects the spin-Hamiltonian parameters for VO(acdc)₂ and Cu(acdc)₂. From the anisotropic spectra (*g*) = 1/3(*g*_∥ + 2*g*_⊥) and ⟨*A*⟩ = 1/3(*A*_∥ + 2*A*_⊥) were calculated and compared with *g*₀ and *A*₀ obtained from the solution spectra. The parameters ⟨*g*⟩ and ⟨*A*⟩ were very close to *g*₀ and *A*₀ values for both complexes in acetone and dimethyl sulfoxide but not in 3-methylpyridine. This latter effect is probably due to adduct formation by the heterocyclic base. Due to the limited solubility of these compounds in various solvents, solvent effects were not further explored.

It is well-known that metal-sulfur bonding is more covalent

Table II. ESR parameters for Cu(acdc)₂ and VO(acdc)₂

Metal complexes	Solvent or host metal ion	g_0	$\langle g \rangle^a$	g_{\parallel}	g_{\perp}	A_0^b	$\langle A \rangle$	A_{\parallel}	A_{\perp}
Cu(acdc) ₂	Acetone	2.047				73			
	Dimethyl sulfoxide	2.046				75			
	3-Picoline	2.058				63			
Cu(acdc) ₂	1% doped in Ni(II) ^c		2.045	2.089	2.023		78	158	38
	3% doped in Ni(II) ^c		2.043	2.082	2.024		78	156	38
	5% doped in Ni(II) ^c		2.042	2.085	2.023		78	156	38
VO(acdc) ₂	Dimethyl sulfoxide	1.970				95			
	3-Picoline	1.976				90			
VO(acdc) ₂	3% doped in Ni(II)		1.968	1.961	1.971		92	159	58
	5% doped in Ni(II)		1.970	1.958	1.976		92	160	57

^a $\langle g \rangle = 1/3(g_{\parallel} + 2g_{\perp})$ and $\langle A \rangle = 1/3(A_{\parallel} + 2A_{\perp})$. ^b All A values are in 10^{-4} cm^{-1} units. ^c Dopings are into the corresponding diamagnetic nickel(II) complex.

Table III. ESR Data for Cu(acdc)₂ and CuN_{4-n}S_n Chromophores^a

Parameter	CuS ₄	Cu-(acdc) ₂	CuN ₂ S ₂	CuN ₄
g_0	2.042-2.045	2.043	2.040-2.061	2.090-2.108
$A_0 \times 10^4 \text{ cm}^{-1}$	75-82	74	90	84-102
g_{\parallel}	2.082-2.087	2.086	2.160-2.129	2.169-2.177
g_{\perp}	2.023-2.035	2.023	2.020-2.060	2.054-2.067
$A_{\parallel} \times 10^4 \text{ cm}^{-1}$	154-165	157	187-193	202-218
$A_{\perp} \times 10^4 \text{ cm}^{-1}$	37-51	39	45	14-16

^a Data for CuS₄, CuN₂S₂, and CuN₄ chromophores were collected from the references cited in the text.

than metal-oxygen or metal-nitrogen bonding.¹⁴ Kivelson and Neiman¹⁵ pointed out that g_{\parallel} values for Cu(II) complexes are a moderately sensitive function of metal-ligand covalency. For ionic environments g_{\parallel} is normally 2.3 or larger and for more covalent environments it is less than 2.3. Recent theoretical work by Smith¹⁶ seems to confirm this view. The g_{\parallel} value of 2.086 for Cu(acdc)₂ is decidedly indicative of a strongly covalent environment. The ESR parameters for Cu(acdc)₂ are very similar to those reported by Weeks and Fackler¹⁷ for bis(diethyldithiocarbamate)copper(II). ESR parameters characteristic of CuS₄, CuN₂S₂, and CuN₄ chromophores^{14,17-30} are compared with those for Cu(acdc)₂ in Table III. It is noted that A_{\parallel} and g_{\parallel} values vary almost linearly with the number of sulfur atoms bound to copper and the values can be approximately expressed by

$$g_{\parallel} = 2.085 + 0.0202(4 - n) \quad (2)$$

$$A_{\parallel} = 160 + 12.6(4 - n) \quad (3)$$

where n is the number of sulfur atoms and A_{\parallel} is in 10^{-4} cm^{-1} units. The data for Cu(acdc)₂ give strong support for the CuS₄ chromophore—structure II for the complex. Using the approach described by Bereman^{18,28} the K (Fermi contact term) and P ($=g_0 g_n \beta_e \beta_n \langle r^{-3} \rangle$) parameters were found to be 0.551 and 0.0132 cm^{-1} , respectively. The P value of 0.0132 cm^{-1} is only 37% of the free ion value (0.0360 cm^{-1}) and it reflects the highly covalent nature of the metal-ligand bonding.

Extensive ESR data for vanadyl(IV)-sulfur-other donor ligated species are not available but spectra for VOS₄ chromophores^{9,26,27,30,32-36} show that isotropic g and nuclear hyperfine splitting, A , values of 1.98 and $\sim 90 \text{ G}$, respectively, can be expected. Other chromophores can be expected to exhibit larger A values and smaller g factors. The data in Table II are fully consistent with the g vs. A plot of Petrakis and coworkers³² for VOL₄ chromophores and structure II proposed for the complexes with the acdc ligand. As noted earlier, the VO(acdc)₂ complex, although it can be isolated and successfully doped into the stable diamagnetic nickel(II) analog, is not particularly stable. Completely satisfactory analyses were never obtained for the complex but the ESR data strongly

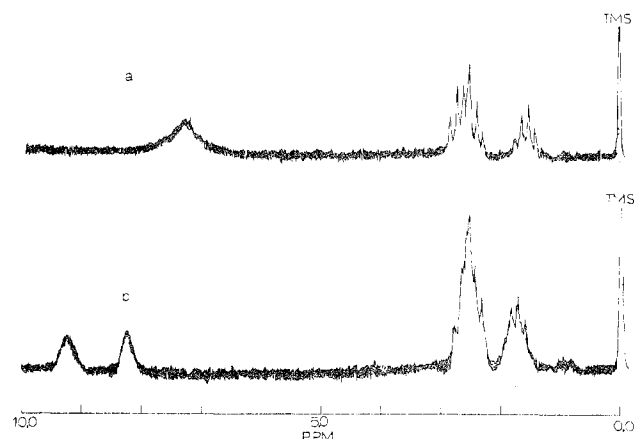


Figure 3. PMR spectra of NH₄acdc (a) and Ni(acdc)₂ (b) in DMSO-*d*₆.

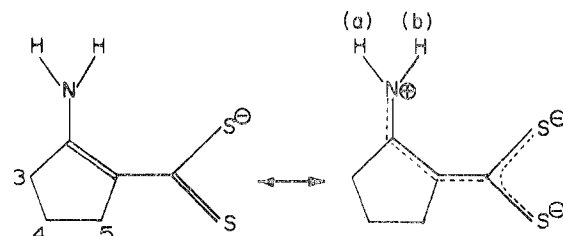


Figure 4. Numbering system and delocalization scheme for the acdc anion.

support the existence of the compound as formulated. Apparently, oxidation to a diamagnetic vanadium(V) species occurs in the presence of moist air. No attempt was made to prepare VO(acdc)₂ under air-free conditions.

Proton NMR Spectra. The relatively high solubility of NH₄acdc and the modest solubilities of the diamagnetic complexes in perdeuterated dimethyl sulfoxide, DMSO-*d*₆, enabled proton NMR spectra to be obtained. The spectrum of NH₄acdc (Figure 3a) shows two multiplets with centers at 1.5 and 2.3 ppm which are assigned to CH₂ proton resonance signals and one broad singlet at 7.13 ppm which is assigned to the NH₂ proton signal. The intensity ratio is approximately 2:4:2 which is consistent with the CH₂ protons at the C₃ and C₅ positions (Figure 4) having about the same chemical shifts, experiencing more shielding than protons at the C₄ position. Most of the metal complexes with the acdc anion exhibit similar spectra (Table IV) for the CH₂ signals but the NH₂ absorption is split in two, the peaks having a 1:1 intensity ratio. The spectrum of Ni(acdc)₂ is shown in Figure 3 where it is apparent that the NH₂ protons are magnetically different with the spectrum having an intensity distribution 2:4:1:1. The position of the chemical shifts and the observation of unequal shifts for the two NH₂ group protons show these systems are very analogous in the behavior to 1-methylcytosine and its hydrochloride salt in dimethyl sulfoxide.^{37,38} Delocalization

Table IV. Proton NMR Data for Compounds in DMSO-*d*₆^a

Compd	CH ₂ protons ^b		NH ₂ protons ^c
	C ₄ (m)	C ₃ and C ₅ (m)	
NH ₄ acdc	1.50	2.53	7.25
Ni(acdc) ₂	1.67	2.50	7.99, 9.10
Cd(acdc) ₂	1.65	2.63	8.75, 8.90
Zn(acdc) ₂	1.62	2.57	8.90, 8.97
Hg(acdc) ₂	1.63	2.60	9.32
In(acdc) ₃	1.67	2.57	8.31, 9.32

^a The chemical shifts are expressed in ppm. TMS was used as an internal standard; m indicates a multiplet. ^b See Figure 4 for numbering scheme. ^c For NH₄Br the PMR chemical shift is 7.30 ppm.

of the lone-pair electrons of the nitrogen atom can bring forth double-bond character in the N-C bond (Figure 4). Magnetic inequivalence of the NH₂ protons in the metal complexes can then arise from hindered rotation of the amino group. Since the presence of a formal charge near a magnetic nucleus can lead to substantial shielding or deshielding, it is not surprising that the separation between the amino absorptions can vary considerably with the metal ion. Separation between the two NH₂ proton signals in Ni(acdc)₂ and In(acdc)₃ are 1.10 and 1.00 ppm, respectively. For Zn(acdc)₂ and Cd(acdc)₂ the separation is small (~0.10 ppm) whereas Hg(acdc)₂ shows only a single broad peak. The chemical shift differences for the NH₂ protons are smaller for the complexes expected to have a tetrahedral geometry than those with planar or octahedral geometries. It is noted that the data for the mercury complex are also consistent with the acdc anion behaving in a monodentate manner, presumably with only one of the sulfur atoms attached to the metal ion.

The NMR data discussed above provide further support for structure II advanced for acdc complexes, particularly for the planar complexes for which the amino protons would be expected to be magnetically equivalent (structure I).

Infrared Spectra. Three or more bands in the 3400–3000-cm⁻¹ region were observed for all of the compounds. The ammonium salt shows bands at 3390, 3260, and 3080 cm⁻¹ with the latter band being attributed to the NH₄⁺ ion. The bands at 3390 and 3260 cm⁻¹ have been assigned⁷ to asymmetric and symmetric NH₂ stretching frequencies. Shifts of these bands to lower frequencies were generally observed upon coordination. In the absence of other data this was taken⁷ to indicate NH₂ coordination. However, it is well known that electronic effects can profoundly influence N-H stretching frequencies and conjugation of the amino group with the cyclopentene ring (Figure 4) could lead to a similar result. If coordination results in an increase in the C-N π-bond order and a concomitant decrease in the π-electron density on the nitrogen atom, the shift of the N-H stretching frequencies (ν(NH)) to lower wave numbers is expected. Mason³⁹ has demonstrated that there is a correlation between ν(NH) and π-electron densities calculated using Hückel molecular orbital (HMO) theory, ν(NH) decreasing with decreasing π-electron density.

Tentative assignments for the infrared spectra of acdc complexes have been discussed by Pattnaik and Sen⁷ and that discussion need not be repeated here. The plethora of bands assignable as NH stretching frequencies suggests inequivalent NH₂ sites in the solid state or considerable coupling of vibrational modes. Our attempts to deuterate the samples yielded new bands in the region of 2400 cm⁻¹ but did not shed any light on the assignments. Considerable further study is needed before the vibrational spectra can be assigned with any degree of certainty. It is noted, however, that bands in the region 300–400 cm⁻¹ occur upon complexation which can be attributed to metal-sulfur stretching frequencies. Unfortu-

Table V. Electronic Spectra of Metal 2-Amino-1-cyclopentene-1-dithiocarboxylates

Compd	Solvent	ν _{max} , kK	10 ⁻⁴ ε	Tentative assignment
NH ₄ acdc	CHCl ₃	25.57	1.12	π* ← n ^a
		32.71	2.13	π* ← π
Ni(acdc) ₂	DMSO	18.62	2.89	¹ B _{1g} ← A _g ^b
		19.13 sh		¹ B _{3g} ← ¹ A _g , ¹ B _{1g} ← ¹ A _g
		26.88	5.67	π* ← n
		35.09	1.40	π* ← π
Cu(acdc) ₂	DMSO	23.15	3.24	² B _{1g} ← ² B _{2g}
		24.14 sh	3.00	² B _{1g} ← ² B _{3g}
VO(acdc) ₂	DMSO	25.30		π* ← n
		33.78 sh		π* ← π
		37.04		Charge transfer
In(acdc) ₃	DMSO	25.19	1.77	π* ← n
Zn(acdc) ₂	DMSO	25.44	2.01	π* ← n
		29.25	0.57	Charge transfer
Hg(acdc) ₂	DMSO	24.88	5.09	π* ← n
		28.99	3.06	Charge transfer
		35.36	4.31	π* ← π
Cd(acdc) ₂	DMSO	25.38	6.23	π* ← n
		36.36	0.91	π* ← π

^a Suggested by R. K. Gosavi and C. N. R. Rao, *Can. J. Chem.*, 45, 1897 (1967). ^b J. D. Lebedda and R. A. Palmer, *Inorg. Chem.*, 11, 484 (1972).

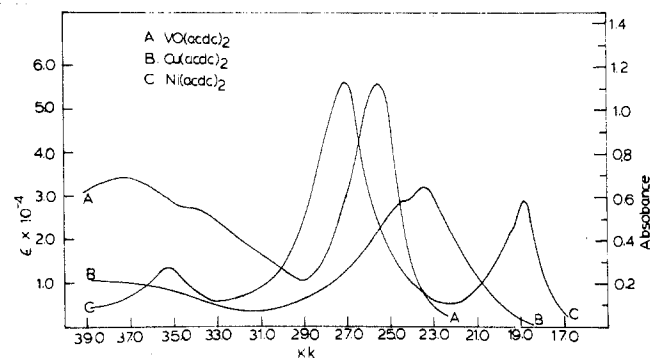
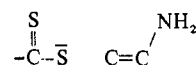


Figure 5. Electronic spectra of metal-acdc complexes in dimethyl sulfoxide. For VO(acdc)₂ an absorbance scale is employed since the concentration could not be accurately determined.

nately, these assignments are not without ambiguities.

Electronic Spectra. Ammonium 2-amino-1-cyclopentene-1-dithiocarboxylate contains two chromophore systems



and exhibits two distinct absorption bands with very high intensity—one at 25.57 kK (1 kK = 1000 cm⁻¹) which can be assigned as the π* ← n band of the thiocarbonyl group and another at 32.71 kK which may be a π* ← n thiocarbonyl band or the result of conjugation between the chromophores. Quite similar absorption spectra are exhibited by the complexes of the d¹⁰ metal ions. The position of the π* ← n transition is practically unchanged whereas more significant changes occur in the ultraviolet region. The new shoulders at about 29 kK observed for the Zn, Cd, and Hg complexes may be the result of a blue-shifted π* ← π transition as suggested for zinc dithiocarbamate complexes.⁶ A charge-transfer origin for the shoulder at ~29 kK is also a possibility. Table V summarizes the electronic spectral data.

Figure 5 shows the electronic spectra of VO(acdc)₂, Cu(acdc)₂, and Ni(acdc)₂. The solution spectra of Cu(acdc)₂ and Ni(acdc)₂ are virtually the same as the mull (transmission) spectra indicating that structural change does not occur in DMSO solution. The band at 23.15 kK in the Cu(acdc)₂ complex is probably due to "d-d" transitions which have acquired appreciable intensity due to the delocalized nature

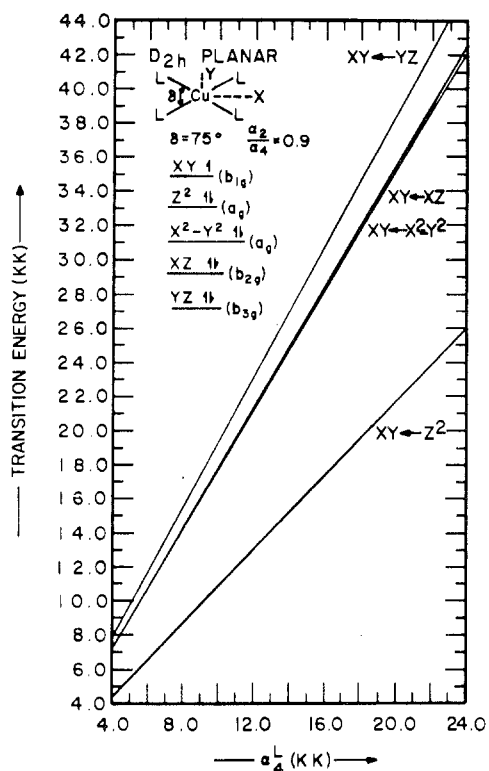


Figure 6. Transition energies for a CuL_4 complex with D_{2h} planar geometry as a function of the α_4 crystal field parameter.

of the bonding in the complexes.⁴⁰

The electronic spectrum of the planar $\text{Ni}(\text{acdc})_2$ complex appears to be unaffected by changes in solvent coordinating power since the mull spectrum and the spectra in acetone, chloroform, and DMSO are essentially identical. This is a common situation with planar NiS_4 chromophores.⁴¹ The high-intensity, low-wave-number bands are also in keeping with structure II. The bands at 18.62 and 19.13 kK of $\text{Ni}(\text{acdc})_2$ can be assigned to "d-d" transitions by analogy with the spectra of other NiS_4 chromophores.^{6,40-46} The spectrum of $\text{Ni}(\text{acdc})_2$ is very similar to previously reported spectra of nickel(II) dithiocarboxylates.⁴³

The electronic spectrum of $\text{Cu}(\text{acdc})_2$ closely resembles those reported for copper(II) dithiocarbamates⁴⁷ and copper(II) cyclopentadienedithiocarboxylate.¹⁸ The spectrum is interpretable in terms of a planar D_{2h} CuS_4 chromophore. Assuming an S-Cu-S angle of 75° , an angle close to those found⁴⁸ for Cu(II) dithiocarbamates, phenomenological crystal field calculations were performed using the previously detailed method.^{49,50} Figure 6 shows the resulting energy level scheme and electronic transition energies as a function of α_4 ($=6Dq$) for the four identical ligands around the Cu(II) ion. The energy level sequence $xy \gg z^2 > x^2 - y^2 > xz > yz$ is at variance with other energy level schemes proposed⁵¹ for D_{2h} chelates but does agree with the energy sequence calculated by Hitchmann⁵¹ using the angular overlap model for copper(II) β -diketonates. The transitions at 23.15 and 24.14 kK are identified with the $b_{1g} \leftarrow b_{2g}$ and $b_{1g} \leftarrow b_{3g}$ ($b_{1g} \leftarrow a_g$) promotions, respectively. The calculations indicate that in the α_4 region of interest (~ 12.2 kK) the separation between the two observable transitions is hardly sufficient to observe resolution as is found experimentally. No evidence was found for the calculated low-energy $b_{1g} \leftarrow a_g$ excitation nor has any been reported for copper(II) dithiocarbamates.⁴⁷ Bereman,¹⁸ however, has noted bands at 11.0, 23.5, and 25.6 kK in his copper(II) cyclopentadienedithiocarboxylate complex which are amenable to the preceding interpretation. The weak intensity of $b_{1g} \leftarrow a_g$ at ~ 12 kK is not unexpected since the

vibronic mechanism also plays an important role in the "d-d" transitions achieving intensity as do low-lying charge-transfer states.⁵² The $b_{1g} \leftarrow a_g$ transitions are allowed by in-plane stretching and bending vibrations in x and y polarization and by out-of-plane bending modes in z polarization. These metal-ligand modes may be expected to lie at lower wave numbers than in related CuO_4 chromophores and hence be less effective in giving rise to observable band intensities. As Belford⁵² has noted, the A_u , B_{2u} , and B_{3u} charge-transfer states are of significance in achieving observable band intensities. Within a perturbation theory context the charge-transfer states may be considered to contribute in a manner inversely proportional to the energy difference with the state of interest. The calculations based on the crystal field model and the observed spectrum of $\text{Cu}(\text{acdc})_2$ suggest the influence of the charge-transfer states will be minimal for the lowest energy $b_{1g} \leftarrow a_g$ excitation. The foregoing suggests that special efforts need be made to find the $xy \leftarrow z^2$ transitions of CuS_4 chromophores. Such a study has recently been completed⁵³ for a variety of copper(II) dithiocarbamates in which the $xy \leftarrow z^2$ transitions are found as comparatively weak shoulders at ~ 16.3 kK. While having some features in common with the spectrum of oxobis(dimethylarsinato)vanadium(IV)³³ assignments for the electronic spectrum of the unstable $\text{VO}(\text{acdc})_2$ complex in fresh DMSO solution are rendered difficult by the absence of low-energy bands which can be assigned in the conventional manner; hence, we have the tentative assignments listed in Table V.

Concluding Remarks

The present data do not answer all questions which might be posed concerning the structures and geometries of the complexes. The limited solubilities of the complexes in common solvents suggest associated, if not polymeric, structures. Detailed structural data will, of course, have to be obtained by crystallographic methods. The behavior of the acdc ligand itself in solution poses a problem. Thomas and Poveda,⁸ who employed equimolar ethanol-water solutions of NH_4acdc and the metal ions in their syntheses, found Co(II) and Ni(II) compounds with the proposed structure III. They suggested the Ni(II) complex was initially a tris species, as claimed in the spectrophotometric determination of Ni(II) with the acid Hacdc ,⁵⁴ which decomposed to yield the structure III compound. Our stoichiometric syntheses in ethanol yielded complexes in agreement with those of Pattnaik and Sen.⁷ It seems plausible that the different complexes obtained with NH_4acdc are due to decomposition of the ligand in water. Our repeated attempts to prepare $\text{Na}(\text{acdc})$ and Kacdc by reaction with the alkali hydroxides in water or absolute ethanol were without success. Such decomposition of dithiolate ligands is not without precedent.⁵⁵ Another discrepancy between our work and that of Thomas and Poveda⁸ is that our $\text{Cu}(\text{acdc})_2$ complex is decidedly of the paramagnetic CuS_4 type whereas their complex is diamagnetic. An alternate formulation for their compound could be $\text{Cu}(\text{acdc})\cdot\text{Hacdc}$, i.e., a $\text{Cu}^1\text{-acdc}$ complex containing one adduct molecule of the ligand acid.

In summary, spectroscopic (ESR, ir, electronic, and proton NMR) evidence supports the exclusive use of sulfur atoms by the acdc ligand in metal bonding.

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Registry No. $\text{Ni}(\text{acdc})_2$, 54955-69-0; $\text{Cu}(\text{acdc})_2$, 32647-17-9; $\text{VO}(\text{acdc})_2$, 55145-44-3; $\text{Zn}(\text{acdc})_2$, 32647-18-0; $\text{Cd}(\text{acdc})_2$, 54955-88-3; $\text{Hg}(\text{acdc})_2$, 54955-70-3; $\text{In}(\text{acdc})_3$, 55208-70-3; NH_4acdc , 18521-92-1.

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Raman and Infrared Studies of Complexes of Mercury(II) with Cysteine, Cysteine Methyl Ester, and Methionine

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Raman and infrared spectral data are reported for L-cysteine (free base), L-cysteine hydrochloride monohydrate, bis(cysteinato)mercury(II) hydrochloride hemihydrate [(C₃H₆O₂NS)₂Hg·HCl·1/2H₂O], L-cysteine methyl ester hydrochloride, bis(methyl-L-cysteinato)mercury(II) hydrochloride hydronitrate monohydrate [(C₄H₈O₂NS)₂Hg·HCl·HNO₃·H₂O], bis(methyl-L-cysteinato)mercury(II) dihydrochloride monohydrate [(C₄H₈O₂NS)₂Hg·2HCl·H₂O], D,L-methionine, and bis(methioninato)mercury(II). The results are discussed in terms of metal-ligand bonding for which $\nu(\text{Hg-S})$ (310–316 cm⁻¹) and $\nu(\text{C-S})$ (670–680 cm⁻¹) were found for the cysteine complexes whereas $\nu(\text{Hg-N})$ at 481 cm⁻¹ was observed for the methionine mercury complex. CH₃ symmetrical stretching is assigned to the range 2912–2917 cm⁻¹ because the frequency does not differ significantly in methionine, methionine hydronitrate, and lithium methioninate. The structural features deduced for the solid state are compared to those determined for the same complexes in acidic aqueous solution by ¹H and ¹³C NMR spectroscopy. The bis(methioninato)mercury(II) complex is particularly interesting in that the solid state appears to favor mercury bonding by amino N and carboxyl O whereas in solution, mercurial bonding is localized to the sulfur atom of the methioninate having an extended-chain configuration in which the amino and carboxyl moieties are remote from the mercury atom. For the mercury complexes of cysteine and cysteine methyl ester, mercurial bonding is exclusive to sulfur in both the solid and solvated states.

Introduction

The sulfur-containing α -amino acids are important in the chemistry of biological systems because of their ability to complex with a wide variety of metal ions. Unfortunately, little is known in particular about the nature of mercury complexes of amino acids such as cysteine and methionine, let alone the mechanisms by which mercurial complexes exert toxic effects,

undergo biotransformation and are transported.² Until recently, very few mercury complexes of sulfur-containing amino acids had been isolated for characterization. Generally, solution studies have been emphasized to gain insight into the structure of complexes first by means of indirect studies such as polarography³ and potentiometry⁴ and later with proton magnetic resonance (PMR) spectroscopy⁵⁻⁸ to obtain structural