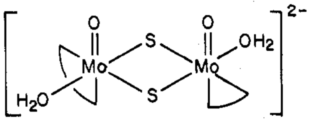
An x-ray crystallographic study of the cesium salt of the di-μ-sulfido complex has been made and the structure is as illustrated.[9] This is similar to that previously determined for



$[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$.[10] Each oxalate ligand occupies coordination sites cis and trans to the terminal oxo ligand, and the Mo–O(oxalate) bond lengths are all identical. Assuming the same structure is retained in solution, complex formation involves replacement of an equatorial H_2O ligand by NCS^-. The possibility of intramolecular rearrangement of the Mo coordination spheres in solution has been noted following ^{13}C NMR experiments (see note, ref 3). There is no evidence as yet for such changes affecting interpretation of kinetic data, e.g., ref 3. Substitution of H_2Os cis to the terminal oxo ligands (probably by an I_d mechanism) has been suggested for the aquo ions VO^{2+}, $Mo_2O_4^{2+}$, and TiO^{2+} [11] and would seem to provide a self-consistent interpretation with that for $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ if the H_2O's of the latter also occupy cis positions. In other words small amounts of the trans form *may* be present in solution but do not obviously contribute to the kinetics. Extreme caution is required here, however.

Although equilibrium constants for 1:1 complexing to both the di-μ-sulfido and di-μ-oxo complexes are of similar magnitude (see above), rate constants k_f and k_b are more rapid, both by a factor of ca. 40, in the case of the di-μ-sulfido complex. These differences originate largely in the enthalpies of activation which are more favorable by 3.7 kcal mol^{-1} (k_f) and 5.0 kcal mol^{-1} (k_b) for the di-μ-sulfido complex, Table II. The labilizing effect of S as compared to O bridges can be accounted for in terms of different bonding characteristics of these ligands. Spivack and Dori[2] have observed that the sulfido bridges in the di-μ-sulfido aquo ion $Mo_2S_2O_2^{2+}$ are extremely inert to cleavage even in concentrated acid. The di-μ-oxo $Mo_2O_4^{2+}$ aquo ion on the other hand undergoes bridge cleavage in HCl > 7 M to yield mononuclear complexes. This different behavior is attributable to strong Mo–S bonding which reduces the availability of electron pairs on the sulfur for protonation as a preliminary to bridge cleavage. The same Mo–S bonding is presumably responsible for the labilizing effect identified in this study. The Mo(V) atoms cannot donate π electrons to the S ligands since metal–metal bond formation[4] has already accounted for the single d electron on each metal. The strong Mo–S bonding must therefore originate from σ and possibly π ligand to metal donations. The former would be expected to give a trans labilizing effect which is possibly enhanced (i.e., atoms drawn closer together) by the π bonding. Since the H_2O's in each Mo coordination sphere of $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$ are trans to one bridging sulfide and cis to the other, it is not possible to specify the position being labilized.

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Registry No. NCS^-, 302-04-5; $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$, 64130-27-4; $Na_2[Mo_2O_4(L\text{-cyst})_2]$, 64091-82-3; $Na_2[Mo_2O_2S_2(L\text{-cyst})_2]$, 30917-53-4; $Cs_2[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]$, 64091-81-2.

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Contribution from the Department of Inorganic Chemistry,
Indian Association for the Cultivation of Science,
Calcutta 700032, India

Metal Complexes of Sulfur–Nitrogen Chelating Agents. 7. *N,N'*-Ethylenebis(methyl 2-amino-1-cyclopentenedithiocarboxylate) Complexes of Ni(II), Pd(II), Co(II), and Cu(II)

S. K. Mondal, D. S. Joardar, and K. Nag*

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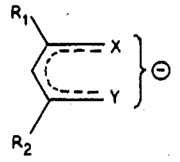
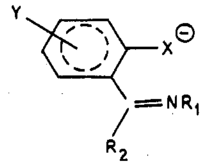
Investigations on stereochemical nonrigidity in tetracoordinated metal(II) chelates from the β-difunctional ligand systems I and II in terms of planar ⇌ tetrahedral equilibrium



I

X = Y = NR, O, S, Se
X = O; Y = NR, S
X = S; Y = NR



II

X = O, S; Y = noncoordinating ring substituents

in noncoordinating solvents have been the subject matter of great interest.[1] A comparative study with bis(β-aminothione) and bis(β-ketoamine) complexes revealed[2] that sulfur exerts a relatively greater stabilization of planar stereochemistry than does oxygen. In connection with our studies on NiN_2S_2 complexes from 2-amino-1-cyclopentenedithiocarboxylic acid, its *N*-ethyl derivative, and its *S*-alkyl ester we have observed[3-5] that only the spin-paired species exist both in the solid state and in solution.

It is interesting to note that although extensive studies have been made on metal complexes derived from the related tetradentate N_2O_2 donors,[6] similar studies with corresponding N_2S_2 donor sets are scanty. The fact that *N,N'*-ethylenebis(salicylideniminato)cobalt(II) and *N,N'*-ethylenebis(acetylacetoniminato)cobalt(II) chelates in the presence of DMF, DMSO, and some other Lewis bases reversibly add molecular oxygen[7,8] provided much stimulus for their investigation as model oxygen carriers.[9] It is expected that the thio analogues may also have similar interesting features. Indeed quite recently metal(II) chelates of *N,N'*-ethylenebis(monothioacetylacetonimine)[10] and *N,N'*-ethylenebis(*o*-mercaptobenzaldiimine)[11,12] have been investigated. We wish to report

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Table I. Analytical Data

		% C		% H		% N		% M	
Compd	Color	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$C_{16}H_{24}N_2S_4$	Yellow	51.61	51.45	6.45	6.55	7.52	7.77		
$C_{16}H_{22}N_2S_4Ni$	Green	44.78	44.55	5.13	5.20	6.53	6.58	13.70	13.80
$C_{16}H_{22}N_2S_4Pd$	Orange	40.30	40.46	4.97	4.70	5.88	5.77	22.33	22.25
$C_{16}H_{22}N_2S_4Co$	Maroon	44.75	44.63	5.12	4.98	6.52	6.45	13.74	13.94
$C_{16}H_{22}N_2S_4Cu$	Red	44.29	44.50	5.07	5.00	6.46	6.35	14.65	14.58

Table II. Infrared Data

Ligand	NiL	PdL	CuL	CoL	Assignments
1580 (s)	1560 (s)	1562 (s)	1570 (s)	1565 (s)	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$
1565 (s)					
1405 (w)	1420 (w)		1420 (w)	1415 (w)	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$
1320 (m)	1310 (m)	1300 (w)	1302 (m)	1300 (m)	$\nu(\mathrm{SCH_3})$
1302 (m)					
1260 (s)	1280 (s)	1275 (m)	1280 (s)	1280 (s)	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N}) + \nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$
1230 (m)	1212 (m)	1210 (w)	1210 (m)	1210 (w)	
1210 (w)					
1030 (w)	1085 (w)	1070 (w)	1070 (m)	1070 (m)	
1000 (m)	1010 (w)	1005 (w)		1002 (w)	
960 (w)	975 (w)	963 (w)	965 (w)	965 (w)	$\mathrm{CH_2}$ rocking
940 (m)	940 (m)	940 (w)	935 (m)	935 (m)	
910 (s)	910 (s)	903 (s)	902 (s)	900 (s)	$\nu_{\mathrm{asym}}(\mathrm{CSSCH_3})$
			890 (s)		
820 (m)	820 (w)		820 (w)	815 (w)	
760 (m)	790 (w)		790 (w)	790 (w)	
730 (m)	720 (w)	720 (w)	720 (w)	720 (w)	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$
580 (w)	570 (m)	570 (m)	565 (m)		
	520 (w, b)	515 (w)	520 (w)	520 (w)	$\nu(\mathrm{M{-}N})$
430 (w)	450 (w)	450 (sh)	440 (b)	450 (b)	

here that another interesting series of metal(II) chelates can be readily generated from *N*,*N'*-ethylenebis(methyl 2-amino-1-cyclopentenedithiocarboxylate).

Table III. Proton Magnetic Resonance Data[a]

Compd	4-CH_2	*S*-CH_3		3,5-CH_2	-CH_2-CH_2-	Hydrogen-bonded proton
Ligand[b]	1.82	2.58		2.78	3.62	~11.5
NiL[c]	1.80		2.53[d]		3.22	
PdL[c]	1.85		2.52[d]		3.20	

[a] Chemical shifts are in ppm (δ). [b] In CDCl. [c] In DMSO-d_6. [d] Center of gravity of broad complex multiplet.

Experimental Section

The ligand was prepared according to Bordás et al.[13] and was purified by recrystallizing twice from benzene (mp 205–207 °C (lit. 210–213 °C)).

Preparation of Metal Chelates. Typically the Ni(II) chelate was obtained by slowly adding a methanolic solution (30 mL) of hydrated nickel chloride (2 mmol) and 2 g of ammonium acetate to a solution of freshly recrystallized ligand (2 mmol) in hot benzene (50 mL). The solution was refluxed for 1 h during which shining crystals began to separate. After cooling of the mixture to room temperature, the compound was filtered and washed first with a small portion of benzene and then with methanol and water. For preparing the Pd(II) chelate potassium tetrachloropalladate and for Co(II) and Cu(II) chelates their acetates in methanol were used. In the case of Co(II), complex solvents were deaerated and the preparation was carried out in nitrogen atmosphere. All compounds were recrystallized from chloroform and the yields obtained were in the range 50–70%.

Analysis. Carbon, hydrogen, and nitrogen were analyzed by Mrs. C. Dutta in the Microanalytical Laboratory of this institute and the metals were estimated by the usual procedures.[14]

Physical Measurements. The electronic spectra of the complexes in solution and in Nujol mull were recorded in a Spectro MOM 201 spectrophotometer. The infrared spectra were recorded with a Beckman IR-20 spectrometer in the range 4000–400 cm^{-1} in Nujol mull. The ^1H NMR spectra of the ligand in $CDCl_3$ and the Ni(II) and Pd(II) chelates in DMSO-d_6 were recorded in a Varian T-60 spectrometer using TMS as the internal standard. The mass spectrum of the Ni(II) chelate was recorded in a Varian MAT SM1 mass spectrometer at 70 eV (the sample was heated to 220 °C). Conductivity measurements were performed in a Philips PR 9500 conductance bridge. Magnetic moment measurements were made on a Gouy balance. Thermal analyses were carried out with a MOM Derivatograph and powder diffraction patterns were photographed with a Nonius Guinier camera using Cu Kα radiation.

Results and Discussion

The analytical data of the compounds are shown in Table I which indicates the formation of 1:1 chelates. The nonelectrolytic behavior of these compounds is evident from their low Λ_M values (~1 mho cm^2 mol^{-1}) in nitrobenzene. Molecular weight determinations (by depression of freezing point method) in nitrobenzene indicate the monomeric composition of the Ni(II) and Cu(II) chelates.[15] Further confirmation of the monomeric composition of the Ni(II) chelate is obtained from its mass spectral data which show that the molecular ions *m/e* 428 (I = 100) and 430 (I = 65) derived from ^{58}Ni and ^{60}Ni isotopes form the most intense peaks. The fragmentation pattern of the compound is rather complicated but it is certain that initial fragmentations take place only at the peripheral parts of the molecule since the presence of the positive ions devoid of a CH_3 group (*m/e* 413, I = 8), a SCH_3 group (*m/e* 383, I = 5; *m/e* 381, I = 13), and two SCH_3 groups (*m/e* 333, I = 8) could be detected.

The Ni(II) and Pd(II) chelates are diamagnetic. The room-temperature magnetic moment of the Cu(II) complex is 1.93 μ_B and that of Co(II) chelate is 2.02 μ_B. These values suggest square-planar configuration of the chelates although tetragonal distortion cannot be entirely ruled out. However, the powder diffraction pattern of the metal chelates shows that they are isomorphic with the Pd(II) complex which strongly suggests a square-planar configuration.

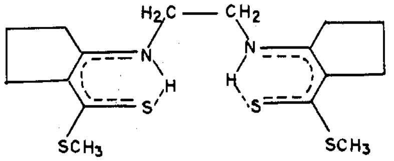
Table II shows the characteristic infrared frequencies of the ligand and its complexes. In the ligand no band due to S–H stretching in the region 2500 cm^{-1} could be observed and N–H stretching appears only as a very weak and broad band at ca.

Table IV. Electronic Spectra

Compd[a]	λ_{max}, cm^{-1}	log ϵ	Assignment
Ligand	25 000	4.43	
	31 250	4.34	
NiL	15 380	2.01	d-d
	22 220	3.76	CT
	30 000	4.29	L-L*
	37 310	4.57	L-L*
PdL	20 410	2.85	d-d
	23 810	3.89	CT
	32 570	4.37	L-L*
CoL	10 530	1.55	d-d
	17 240	2.70	d-d
	21 740	3.77	CT
	30 120	4.11	L-L*
	35 710	4.29	L-L*
CuL	12 270	1.87	d-d
	20 830	3.20	CT
	26 310	4.18	L-L*
	31 440	4.47	L-L*

[a] In chloroform.

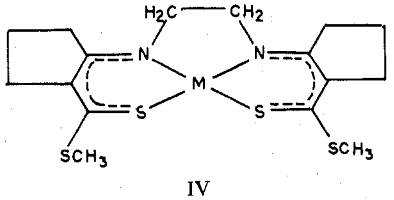
3200 cm^{-1}. This indicates that the ligand has the hydrogen-bonded structure III. The ^1H NMR spectrum of the ligand (shown in Table III) confirms the above structure.



III

The assignment of the infrared bands has been made in accordance with our previous studies.[3-5] It may be noted that the two strong bands at 1580 and 1565 cm^{-1} in the ligand get collapsed to a single band in the chelates which appears to be consistent with the assumption that there is more delocalization of the double bonds in the chelates compared to that in the ligand. The presence of discrete C=C or C=N bonds can be ruled out on the grounds that these vibrations appear at considerably higher energy range, ca. 1650 cm^{-1}. Indeed a similar observation made in tetradentate thioiminato Schiff base complexes has been rationalized by invoking $d\pi$–$d\pi$ interaction of the sulfur donors with metal ions.[10]

A comparison of the ^1H NMR spectral data of the ligand and its Ni(II) and Pd(II) chelates (Table III) reveals that 4-CH_2 protons are least affected due to chelation. On the other hand, the $-CH_2CH_2-$ bridge and SCH_3 and 3,5-CH_2 protons have undergone considerable upfield shift due to chelation. In fact, SCH_3 and 3,5-CH_2 protons get very much overlapped. The stereochemical rigidity in the coplanar form (IV) coupled with electron flow from the metal onto the chelate ring (π back-bonding) induces more electron delocalization which in effect causes better shielding of the protons in the metal chelates.



IV

The electronic spectral features of the compounds are shown in Table IV. In the absence of detailed MO calculation it is difficult for the most part to make definite assignments of the transitions. In the Ni(II) and Pd(II) chelates the bands at 15 380 and 20 410 cm^{-1} respectively are due to a d–d transition which may be due to either $^1A_{1g} \rightarrow {}^1A_{2g}$[14,16] or $^1A_g \rightarrow {}^1B_{1g}$ transition.[17] Although the usual energy range for this band in $[NiN_2S_2]$ chromophores is 18 000 cm^{-1}, however, in both bis(bidentate)[2-5] and tetradentate[10] $[NiN_2S_2]$ complexes, where there is extensive delocalization in the chelate ring, this band is observed in the range 15 000–16 500 cm^{-1} and they behave more like $[NiS_4]$ chromophores in the spectrochemical series. Crystal field stabilization energies Δ_1 evaluated from the relation $E(\nu) = \Delta_1 - 35F_4$ (F_4 = 80 cm^{-1}) are 18 180 and 22 510 cm^{-1} respectively for the Ni(II) and Pd(II) chelates. It may be noted that the energy sequence of the charge transfer band in these two compounds is Ni(II) < Pd(II) which according to Gray[18] may be assigned to M → L charge transfer. The electronic spectrum of the Ni(II) chelate has been examined in the solid state (mull) and in a number of coordinating solvents, e.g., pyridine, DMSO, DMF, etc., and it shows identical spectral features. Thus tetragonal distortion in the solid or the expansion of coordination number through solvent participation appears unlikely. This behavior is identical with malononitriledithiolato type complexes which possess remarkably stable square-planar configuration.[18]

The electronic spectrum of the Co(II) complex shows two bands due to d–d transition and occurs almost in the same energy observed in the corresponding tetradentate thioiminato Schiff base complexes.[10] Chloroform solution of the Co(II) complex apparently reacts with oxygen since the spectrum slowly changes with time. In the Cu(II) chelate d–d transition occurs at rather relatively low energy (12 270 cm^{-1})[19] compared with those normally observed in square-planar complexes.[20] However, in several $[CuN_2S_2]$ square-planar chelates this band has been observed in the range 13 000–14 000 cm^{-1}.[10]

The stable square-planar configurations in the metal chelates are also apparent from their high thermal stability. For example, the Ni(II) complex begins to decompose above 280 °C and the Co(II) complex at 220 °C.

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Registry No. Ligand, 34281-33-9; NiL, 63665-43-0; PdL, 63625-65-0; CoL, 63641-42-9; CuL, 63665-42-9.

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