

Metal Complexes of Sulphur-Nitrogen Chelating Agents : Transition Metal Complexes of the Esters of 2-Amino-1-cyclopentene-1-dithiocarboxylic Acid

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The complexes of Ni(II), Cu(II), Co(II), Cd(II) and Fe(III) with diethylamino-methyl ester of 2-amino-1-cyclopentene-1-dithiocarboxylic acid, $\text{RHNCCH}_2\text{CH}_2\text{CH}_2\text{C}$ -

C(S)S c' [LH when $\text{R}=\text{H}$ and $\text{R}'=\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$] and Ni(II) with methyl ester of N-methyl acid [L'H when $\text{R}=\text{R}'=\text{CH}_3$] have been synthesized and characterized.

CHELATING species containing both soft and hard potential donor centres when complexed to metal ions are of significance due to diverging reasons. In transition metals the electronic structure and stereochemistry of sulphur-nitrogen ligand complexes are comparatively much less understood¹. The added interest in them with reference to main group elements and probably also with early transition metals is due to their preferential bond formation with soft or hard donors resulting into what is now known as ambidentate² character of the ligands. With the above view in mind stereochemistry of some later transition metal complexes of the esters of 2-amino-1-cyclopentene-1-dithiocarboxylic acid, $\text{RHNCCH}_2\text{CH}_2\text{CH}_2\text{CC(S)SR}'$,

has been described in the present paper.

Experimental

All the solvents were purified (dried and distilled) by the standard methods. The esters were prepared by the literature methods^{3,4}. The infrared spectra were recorded on nujol mull on a Perkin-Elmer-621 spectrophotometer (4000-200 cm^{-1}). The pmr spectra were run on A-60 Varian spectrometer in CCl_4 solution using TMS as an internal standard. The magnetic moment measurements were made at room temperature (308° K) by Gouy's balance and electronic spectra were run in CHCl_3 solution on Carry-14 spectrometer. Metal and sulphur analyses were carried out gravimetrically and nitrogen by the Kjeldahl method. The carbon and hydrogen analyses were carried out in our Microanalytical Laboratory. Molecular weights were determined cryoscopically in benzene and nitrobenzene.

General method of the preparation of transition metal complexes of diethylaminomethyl ester of the acid and methyl ester of 2-N-methylamino-1-cyclopentene-1-dithiocarboxylic acid: Methanolic or

ethanolic solutions of metal chlorides or acetates [of Ni(II), Cu(II), Co(II), Cd(II) and Fe(III)] were mixed with the solutions of the ligands in tetrahydrofuran (in case of the diethylaminomethyl ester) and in methanol or ethanol (in case of the methyl ester) in appropriate molar ratios. In the case of chlorides the reactions were facilitated by adding a suitable amount of NaHCO_3 . The metal complexes precipitated were filtered out and washed thoroughly with water. All the compounds (Table I) were recrystallized from hot tetrahydrofuran or methanol and dried under vacuum at 32-35°/0.1 mm/1 hr.

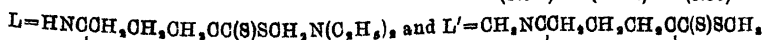
Results and Discussion

The transition metal complexes of the type, $\text{M}[\text{RHNCCH}_2\text{CH}_2\text{CH}_2\text{CC(S)SR}]_n$, [$\text{R}=\text{R}'=\text{CH}_3$, $\text{M}=\text{Ni(II)}$ and $n=2$; $\text{R}=\text{H}$, $\text{R}'=\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$, $\text{M}=\text{Ni(II)}$, Co(II) , Cd(II) , Cu(II) , $n=2$ and $\text{M}=\text{Fe(III)}$, $n=3$] have been synthesized from the corresponding acetates or chlorides. All the complexes are dark coloured crystalline solids with sharp melting points, except of Co(II) and Fe(III) which decomposed, and are soluble only in tetrahydrofuran and nitrobenzene. The complexes of Ni(II) with the methyl ester of 2-N-methylamino-1-cyclopentene-1-dithiocarboxylic acid is soluble in all common organic solvents. All of these are found to be monomeric (cryoscopically).

In the ir spectrum of diethylaminomethyl ester the presence of a broad band of $\nu(\text{N}-\text{H})$ at 3290 cm^{-1} and absence of $\nu(\text{N}-\text{H})$ band in the spectrum of methyl ester show the existence of the following structures (Ia or Ib) which is also supported by the absence of $\nu(\text{S}-\text{H})$ band in the 2550-2650 cm^{-1} region in them⁴. The spectra of both the esters⁴ show strong to medium intensity bands of $\nu(\text{C}=\text{S})$ at 1270 ± 5 , 1155 ± 5 cm^{-1} along with $\nu(\text{C}=\text{N})$ and at 725 cm^{-1} .

TABLE 1—TRANSITION METAL COMPLEXES OF THE ESTERS OF 2-AMINO-1-CYCLOPENTENE-1-DITHIOCARBOXYLIC ACID

Sl. No.	Products* colour	m p. (°C)	Analysis (%) Found (Calcd)					μ_{eff} 308° (B.M.)	Molecular weight Found (Calcd.)
			O	H	M	S	N		
1.	L_2Ni Bright brown	155-57	48.99 (48.61)	7.32 (7.02)	10.26 (10.76)	23.10 (23.51)	10.10 (10.27)	Diamagnetic	568 (545.4)
2.	L_2Cu Dark blue	270-72	48.61 (48.00)	7.48 (7.39)	11.34 (11.54)	23.61 (23.26)	10.08 (10.18)	1.90	574 (550.8)
3.	L_2Co Black	above 360 ^d	—	—	—	23.11 (23.49)	10.42 (10.27)	2.12	571 (545.7)
4.	L_2Cd Olive	320-21	—	—	18.67 (18.33)	21.01 (21.40)	9.18 (9.35)	Diamagnetic	574 (599.2)
5.	L_2Fe Light brown	above 360 ^d	50.89 (50.42)	7.53 (7.31)	7.35 (7.11)	25.25 (24.47)	10.98 (10.69)	5.35	805 (785.9)
6.	L'_2Ni^{**}	133-34	—	—	13.04 (13.63)	30.16 (29.84)	6.67 (6.50)	Diamagnetic	455.6 (430.7)

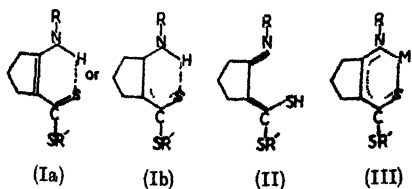
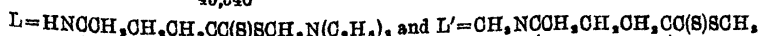


* Crystalline solids, yields, 85-90%. Molecular weights were determined for the compounds Sl. No. 1-5 in nitrobenzene and for Sl. No. 6 in benzene cryoscopically.

** PMR values (in ppm) for SCH_2 (2.63), 3,5- CH_2 (2.90), 4- CH_2 (1.95) and NCH_2 (3.15).

TABLE 2—ELECTRONIC SPECTRAL DATA (in cm^{-1}) OF THE TRANSITION METAL COMPLEXES

LH	L/H	L_2Ni	L_2Cu	L_2Co	L_2Cd	L_2Fe	L'_2Ni	Assignments
25,510	25,252			11,430] $\pi-\pi^*$
30,769	31,545					11,525		
38,168		16,000	16,667	16,000			16,100	d-d d-d($^1A_{1g} \rightarrow ^4T_{1g}$) d-d($^1A_{1g} \rightarrow ^1A_{1g}$) (MN, S_0 chromophore)
		20,000					21,740	d-d($^1A_{1g} \rightarrow ^1B_{1g}$)
		24,570	30,731	24,510	24,000	24,540	25,126] L-L* (L-M or M-L)
		30,120	32,051	30,080	32,260	30,050	31,444	
		37,037	44,440	37,037	37,037	37,042		
		45,540						



The alternate structure involving (II), appears to be much less probable due to the absence of discrete $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ vibrations which appear at considerably high energy range^{4,5} ca 1650 cm^{-1} . In the metal complexes the bands of $\nu(\text{C}-\text{N}+\text{C}=\text{S})$, $\nu(\text{C}=\text{S}+\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ shift to lower frequency region⁶⁻⁷ by $15-20 \text{ cm}^{-1}$ suggesting invariably the bidentate behaviour of the esters. The characteristic bands of $\nu(\text{C}-\text{C})$, $\nu(\text{C}=\text{C}+\text{C}=\text{N})$ are observed at 1595 ± 5 and $1360 \pm 5 \text{ cm}^{-1}$ respectively^{4,5}. The metal-nitrogen and metal-sulfur frequencies have been seen in the regions $450-525$ and $325-400 \text{ cm}^{-1}$ respectively⁶⁻⁷.

The complexes of Ni(II) and Cd(II) are found to be diamagnetic whereas the complexes of Co(II) and Cu(II) are paramagnetic in nature with magnetic moments 2.12 and 1.90 B.M. respectively.

On the basis of these results the complexes of Ni(II) , Cd(II) , Cu(II) and Co(II) are considered to have definite square-planar configurations. Fe(III) tris complex being octahedral⁸ is found to have magnetic moments 5.35 B.M. which can also be taken as an additional evidence for the absence of S-S bonding in it arising out of the structure (II), since spin crossover behaviour¹ associated with S-S ligands decreases the magnetic moment to the order of 4.0 B.M. The somewhat lower magnetic moments in the Fe(III) complex in comparison to the usual high spin value (5.7-5.9 B.M.) can not be rationalized at the moment until the structure of the complex is determined by single crystal analysis. It may however be mentioned that the magnetic behaviour of the well characterized S-N chelates under octahedral environment is not known⁸. It is from this objective, that we have begun examining the structure of the Fe(III) complex by X-ray analysis.

The esters in their electronic spectra exhibit two or three bands in $25,000-39,000 \text{ cm}^{-1}$ region (Table 2) due to intraligand transitions of the $\pi-\pi^*$ type. The spectra (Table 2) of all the complexes are similar to each other in the ultraviolet region

where absorptions involving the ligands predominate. The bands in the region 24,000-45,000 cm^{-1} have been assigned as either M-L, L-M or ligand transitions^{5,7}. The highly covalent character of the metal donor bonds of the metal chelates is evidenced⁶ by the dissimilarity between the spectra of the free esters and the metal chelates. The presence of the bands in the region 16,000-16,700 cm^{-1} assignable to MN_2S_2 chromophores (d-d) in the complexes of Ni(II)^{5-7,9}, Cu(II)^{6,10,11} and Co(II)^{5,6,12} is strong evidence for the delocalization in the ring and also for their square-planar geometry. In Fe(III) octahedral complex a band at 11,525 cm^{-1} has been observed due to d-d transitions⁸.

The complexes of dichylaminomethyl ester could not be scanned for pmr spectra due to poor solubility. The spectrum of the Ni(II) compound with the methyl ester exhibits a slight upfield shift^{6,7} in the signals for SCH_3 , 3,5- CH_3 and NCH_3 protons whereas 4- CH_3 protons remain at the same position in comparison to the ligand⁴. Surprisingly, N-methyl protons appear as doublet (centred at 3.15 ppm) which defy interpretation except in terms of the two environmentally different positions of the methyl group with respect to the chelate ring.

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References

1. M. F. MACKAY, M. J. O'CONNOR, P. J. OLIVER, K. S. MURRAY and P. J. NEWMAN, *Inorg. Nuclear Chem. Lett.*, 1977, **13**, 417.
2. J. L. K. F. DE VRIES and R. H. HERBER, *Inorg. Chem.*, 1972, **11**, 2458.
3. T. TAKESHIMA, M. YOKOYAMA, T. IMAMOTO, M. AKANO and H. ASABA, *J. Org. Chem.*, 1969, **34**, 730.
4. B. BORDAS, P. SOHAR, G. MATOLCSY and P. BERENCSEI, *J. Org. Chem.*, 1972, **37**, 1727.
5. D. S. JOARDAR, S. K. MONDAL and K. NAG, *Inorg. Chem.*, 1978, **17**, 191.
6. P. R. BLUM, R. M. C. WEI and S. C. CUMMINGS, *Inorg. Chem.*, 1974, **13**, 450.
7. D. S. JOARDAR, S. K. MONDAL and K. NAG, *Bull. Chem. Soc. Japan*, 1977, **50**, 1489.
8. M. J. M. CAMPBELL, R. GRZESKOWIAK and G. S. JUNEJA, *J. Inorg. Nuclear Chem.*, 1978, **40**, 1247.
9. D. H. GERLACH and R. H. HOLM, *J. Amer. Chem. Soc.*, 1969, **91**, 3457.
10. R. H. HOLM, *J. Amer. Chem. Soc.*, 1960, **82**, 5632.
11. A. OUCHI, M. HYODO and Y. TAKAHASHI, *Bull. Chem. Soc. Japan*, 1967, **40**, 2819.
12. G. W. EVERETT, JR. and R. H. HOLM, *J. Amer. Chem. Soc.*, 1965, **87**, 5266.