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Complexes of Cobalt(II), Nickel(II), Copper(II), and Zinc(II) with the Tripod-Like Ligand Tris (2-methylthioethyl)amine

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The preparation and properties of nine complexes formed by the quadridentate ligand tris(2-methylthioethyl)amine, TSN, and the halides or thiocyanate of cobalt(II), nickel(II), copper(II), and zinc(II) have been studied. The cobalt complexes are formulated as $[CoX(TSN)]_2[CoX_4]$ *thus containing both high-spin five-coordinated cobalt and tetrahedral cobalt. The compounds* $NiX_2(TSN)$ *are octahedral and* $[CuBr(TSN)]Br$ *is five-coordinated. Zinc iodide forms the monomeric compound* $ZnI_2(TSN)$*.*

Introduction

It has been shown recently in several papers that tripod-like quadridentate ligands are particularly capable of forming five-coordinated complexes with transition metals.[1-4] However, there is an important effect related to the bulkiness of the substituents at the donor atoms. If the substituents are small, six-coordinated complexes are formed. For instance, this is case with tris(2-aminoethyl)amine, tren, which forms octahedral complexes at least with nickel(II).[5] On the other hand, the nature of the donor atoms is important in inducing spin-pairing in five-coordinated complexes: hard donors give high-spin complexes whereas soft donors give low-spin complexes.

As a part of a systematic investigation which is being carried on in this Laboratory on five-coordinated high-spin complexes, this paper presents a number of compounds of cobalt(II), nickel(II), copper(II), and zinc(II) with the tripod-like ligand tris(2-methylthioethyl)amine, $N(CH_2CH_2SCH_3)_3$, hereafter called TSN. The ligand is potentially quadridentate with the set of donor atoms NS_3. Thioethereal sulfur is a fairly soft donor atom and indeed the five-coordinated complexes of Meek's ligand $(o-CH_3S-C_6H_4)_3P$, TSP, with nickel halides are low-spin complexes.[2b] However, ligands containing sulfur and nitrogen, such as bis-(2-dimethylaminoethyl)sulfide[6] and bis(2-α-pyridylethyl)sulfide,[7] give high-spin five-coordinated complexes with cobalt(II) and/or nickel(II). The ligand TSN, therefore, has been chosen in order to obtain more information about the spin-pairing ability of thioethereal sulfur.

Experimental Section

Preparation of the Compounds. Dimethylsulfate (115 g.) was added dropwise to a cold suspension of crude tris(2-thiolethyl) amine[8] (60 g.) in aqueous 50% NaOH (80 ml.). The mixture was heated at 60° for 2 hr, cooled, and the oily layer was extracted into ether. The ethereal extract was dried over anhydrous calcium sulfate. After removal of the ether the compound tris(2-methylthioethyl)amine distilled as a yellowish oil, b.p. 136-140° (2 mm.); yield 22 g. (30%).

Anal. Calcd. for $C_9H_{21}NS_3$: C, 45.14; H, 8.84. Found: C, 45.23; H, 8.90.

The cobalt complexes were prepared by adding 12 mmoles of TSN to the hot solution of the appropriate cobalt halide (10 mmoles) in *n*-butanol (40 ml.). All the complexes were recrystallized from hot *n*-butanol containing a few drops of the ligand. They are very slightly soluble in chloroform and insoluble in non-polar solvents. The products have the general formula $3CoX_2 \cdot 2(TSN)$ irrespective of the excess of ligand employed. Under analogous conditions cobalt perchlorate, nitrate, and sulfate do not react with TSN.

Anhydrous nickel halides and nickel thiocyanate (10 mmoles) reacted in warm *n*-butanol (20 ml.) with the ligand (12 mmoles) precipitating on cooling complexes of the general formula $NiX_2(TSN)$. The halide derivatives were recrystallized by dissolving them in chloroform, and adding petroleum ether to the filtered solution which contained a few drops of TSN. They are fairly soluble in benzene, chloroform, nitroethane and insoluble in petroleum ether. The thiocyanate derivative is slightly soluble in nitroethane but almost insoluble in 1,2-dichloroethane.

The chloride and bromide of copper(II) (10 mmoles) dissolved in a 1:1 mixture of ethanol-butanol (30 ml.) reacted at room temperature with TSN (12

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(3) M. Ciampolini and N. Nardi, *ibid.*, 5, 41 (1966).

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(5) D. Hall and M. D. Woulfe, *Proc. Chem. Soc.*, 346 (1958); S. E. Rasmussen, *Acta Chem. Scand.*, *13*, 2009 (1959); R. W. Asmussen and O. Bostrup, *ibid.*, *11*, 1097 (1957).

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(8) J. Harley-Mason, *J. Chem. Soc.*, 320 (1947).

mmoles) precipitating dark green solids. Only the bromide can be obtained in the pure state by recrystallization from butanol-petroleum ether mixtures.

Finally, the reaction mixtures of the zinc halides (10 mmoles) and TSN (12 mmoles) in *n*-butanol (20 ml.) separated as sticky oils. With the bromide and iodide the oils crystallized on long storage at room temperature. The solids were ground with petroleum ether containing a few drops of TSN, collected and dried *in vacuo* at room temperature.

The analytical data are reported in Table I.

Table I. Analytical Data for the Complexes of TSN

Compound	Color	Λ^b $(CH_2Cl)_2$	Λ^b $EtNO_2$	$\bar{n}^c$	%C Calcd.	%C Found	%N Calcd.	%N Found	%H Calcd.	%H Found	%Metal Calcd.	%Metal Found
$[CoCl(TSN)]_2[CoCl_4]$	Amethyst	—	—	—	24.90	24.98	3.22	3.38	4.87	4.99	20.36	19.97
$[CoBr(TSN)]_2[CoBr_4]$	Purple red	—	—	—	19.05	18.98	2.46	2.55	3.73	3.90	15.58	15.30
$[CoI(TSN)]_2[CoI_4]$	Brown	—	—	—	15.25	15.24	1.97	2.00	2.99	2.90	12.47	12.34
$NiCl_2(TSN)$	Light green	2.3	2.6	$1.05^{c'}$	29.29	29.45	3.79	3.79	5.74	5.75	15.90	15.64
$NiBr_2(TSN)^a$	Light green	0.4	3.7	$1.05^{c'}$	23.60	24.10	3.06	3.19	4.62	4.64	12.81	12.88
$NiI_2(TSN)$	Golden brown	1.6	19.0	—	19.58	19.90	2.54	2.67	3.83	4.05	—	—
$Ni(NCS)_2(TSN)$	Blue gray	—	5.4	—	31.88	31.72	10.14	10.05	5.11	5.25	—	—
$[CuBr(TSN)]Br^a$	Dark green	—	56.0	—	23.35	23.58	3.02	3.04	4.57	4.61	13.74	13.57
$ZnI_2(TSN)$	Pink	0.6	18.0	$1.02^{c''}$	19.35	19.27	2.51	2.56	3.79	3.75	11.70	11.68

[a] Sulfur analysis is respectively: $NiBr_2(TSN)$, calcd. 21.00, found 20.77; $[CuBr(TSN)]Br$, calcd. 20.77, found 20.33. [b] Corrected for conductivity of pure solvent. Λ given in units of $cm^2\,ohm^{-1}\,mole^{-1}$. Reference values in 1,2-dichloroethane and nitroethane respectively, are: $[(n\text{—}C_4H_9)_4N]Br$, 19, 70. [c] $\bar{n} = M_{found}/M_{calcd.}$ for *ca.* $2\times10^{-2}\,M$ nitroethane (*c′*) and 1,2-dichloroethane (*c″*) solutions at 37°.

Physical Measurements. The absorption spectra were recorded in the range 5000-30,000 cm^{-1} with a Beckman DK2 spectrophotometer. The solvents were of reagent grade quality and were dried and distilled before use. The diffuse reflectance spectra were measured using the standard Beckman reflectance attachment and magnesium oxide as the reference.

The conductivity values were measured on a WTW Model LBR/B conductance bridge. Concentration of the solutions were approximately $10^{-3}\,M$.

Molecular weights were determined in 1,2-dichloroethane and in nitroethane at 37° with a Mechrolab Model 301 A vapor pressure osmometer calibrated with benzil. The solutions were approximately $2\times10^{-2}\,M$. The results were reproducible ±1%.

The apparatus and the experimental technique used for the magnetic measurements were described in a previous paper.[9]

The infrared spectra were recorded on Nujol mulls using a Perkin-Elmer 337 spectrophotometer.

Results and Discussion

The cobalt complexes, which have the formula $3CoX_2 \cdot 2(TSN)$, exhibit a mean magnetic moment per cobalt atom of 4.45-4.55 B.M. (Table II) which is indicative of a high-spin electronic configuration. Their reflection spectra show four bands at *ca.* 6000, 12,000, 15,000, and 20,000 cm^{-1} (Figure 1; Table III).

These spectra are very similar to those of the high-spin five-coordinated complexes of cobalt(II) having C_{3v} structure like $[CoX(Me_6tren)]X$[3,10] (Figure 1). It must be recalled, however, that the two bands at *ca.* 6000 and 15,000 cm^{-1} are also shown by tetrahedral complex anions CoX_4^{2-} (Figure 1).

A plausible formulation for these complexes, which is also consistent with their insolubility in organic solvents, is $[CoX(TSN)]_2[CoX_4]$. The cobalt(II) should have a high-spin five-coordinated configuration —probably trigonal bipyramidal—in the cationic species, and a tetrahedral structure in the anionic species.

Table II. Magnetic Data for Some Complexes of TSN[a]

Compound	t, °C	$10^6 \times \chi_A$ (c.g.s.u.)	μ_{eff} (B.M.)
$[CoCl(TSN)]_2[CdCl_4]$	14	8620	4.45
$[CoBr(TSN)]_2[CoBr_4]$	23	8670	4.55
$[CoI(TSN)]_2[CoI_4]$	19	8390	4.45
$NiCl_2(TSN)$	13	4320	3.16
$NiBr_2(TSN)$	13	4220	3.12
$NiI_2(TSN)$	17	4160	3.10
$Ni(NCS)_2(TSN)$	20	4060	3.10
$[CuBr(TSN)]Br$	13	1380	1.79

[a] Diamagnetic corrections are (10^{-6} c.g.s.u.): TSN, 166; Cl, 20; Br, 31; I, 45; NCS, 31. B. N. Figgis and J. Lewis, in «Modern Coordination Chemistry», J. Lewis and R. G. Wilkins Ed., Interscience Publishers, Inc., New York, N. Y., p. 403 (1960).

Table III. Electronic Spectral Data of Some Complexes of TSN in the Solid State

Compound	Absorption max. (cm^{-1})
$[CoCl(TSN)]_2[CoCl_4]$	5700, ~11,800 sh, 14,800, ~15,600 sh, 19,500-20,300
$[CoBr(TSN)]_2[CoBr_4]$	5400, ~11,500sh, 14,100, 18,900-19,700
$[CoI(TSN)]_2[CoI_4]$	5200, ~6500 sh, ~10,800 sh, 13,200, 18,200-19,000
$NiCl_2(TSN)$	8900, 14,400, 23,500
$NiBr_2(TSN)$	8900, 14,400, ~19,400 sh, 23,500
$NiI_2(TSN)$	~8700 sh, 9500, 15,000, 23,500
$Ni(NCS)_2(TSN)$	10,500, 16,500, ~25,600 sh
$[CuBr(TSN)]Br$	11,800, 14,800

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(9) L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, *82*, 3487 (1960).

(10) $Me_6tren = N[CH_2CH_2N(CH_3)_2]_3$.

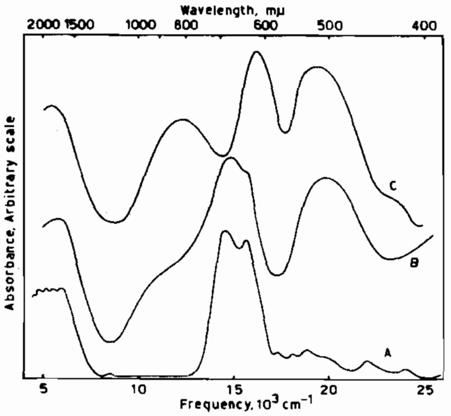

Figure 1. Diffuse reflectance spectra of some complexes of cobalt(II): A, $(Et_4N)_2[CoCl_4]$; B, $[CoCl(TSN)]_2[CoCl_4]$; C, $[CoBr(Me_6tren)]Br$.

The nickel halides give 1:1 complexes with the ligand TSN, which are very soluble in $(CH_2Cl)_2$ and $C_2H_5NO_2$. In these solvents, they are monomeric and non-electrolyte so that they must be formulated as discrete molecules $NiX_2(TSN)$. The isothiocyanate derivative is insufficiently soluble for molecular weight measurement but does not conduct appreciably in 10^{-3} *M* nitroethane solutions. Its infrared spectrum in the solid state shows bands which are characteristic of the CN and CS stretching modes of the isothiocyanate groups;[11] *i.e.* at 2090 and 2070 cm^{-1}, for the CN stretch, and at 805 and 798 cm^{-1}, for the CS stretch. No bands attributable to free, bridging, or S-bonded NCS groups are found.[12]

All of the nickel compounds are high-spin ($\mu = 3.1$ B.M., Table II) and show spectra which are characteristic of an octahedral structure both in solution and in the solid state (Figure 2, Table III). It is worthwile to compare the spectral parameters Dq and $\beta = B(\text{complex})/B(\text{free ion})$ of the complexes $Ni(NCS)_2(TSN)$ and $Ni(NCS)_2(tren)$[13] having the chromophores NiN_3S_3 and NiN_6 respectively. The values are: $Ni(NCS)_2(TSN)$, Dq = 1050 cm^{-1}, $\beta = 0.67$; $Ni(NCS)_2(tren)$, Dq = 1080 cm^{-1}, $\beta = 0.83$. The values of the spectral parameter Dq are in agreement with the fact that the position of the thioethereal sulfur in the spectrochemical series is on the low field side of the amine nitrogen.[14] The low value of the nephelauxetic ratio β in the TSN complex is in accordance with the soft character of thioethereal sulfur.[15]

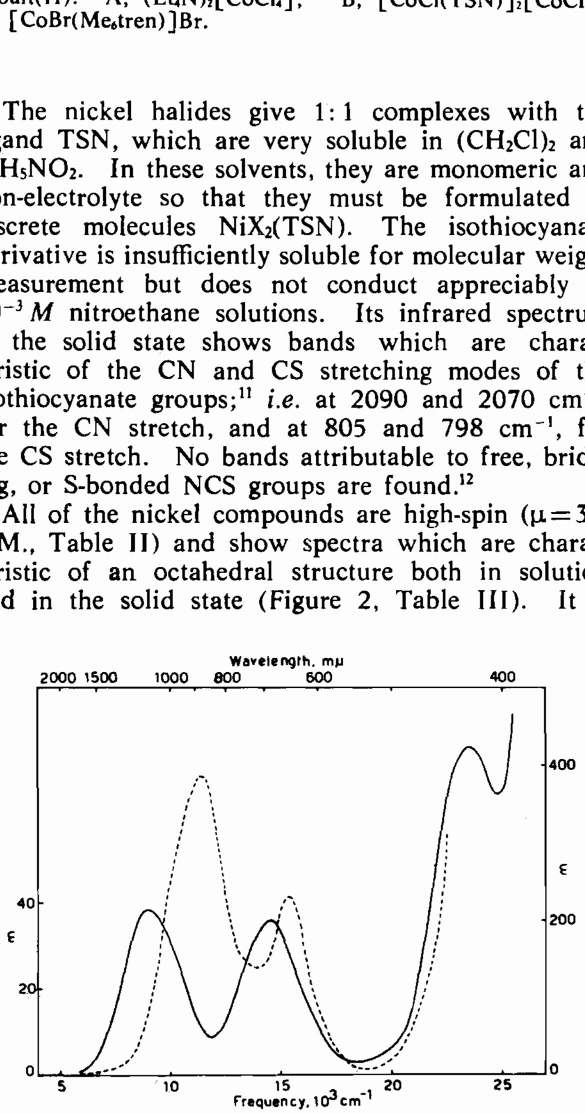

Figure 2. Absorption spectra of some complexes of TSN: $NiBr_2(TSN)$ (solid line, absorbance values on the left scale), $[CuBr(TSN)]Br$ (dotted line, absorbance values on the right scale).

The behaviour of TSN with respect to the nickel is similar to that of the ligand tren, which forms octahedral complexes,[5] and is different from that of the bulkier ligands Me$_6$tren[3] and TSP,[7b] which form only the five-coordinated complexes [MX(ligand)]X.

The only fairly stable complex formed by copper halides and TSN is $CuBr_2(TSN)$. This complex is very soluble in nitroethane and 1,2-dichloroethane where it behaves as an 1:1 electrolyte. Its d–d spectrum shows two bands at 11,400 ($\varepsilon = 390$) and 15,400 cm^{-1} ($\varepsilon = 240$), both in solution and in the solid state (Figure 2; Table III). This spectrum is very similar to that of the trigonal bipyramidal complex $[CuBr(Me_6tren)]Br$, which has two bands at 10,400 ($\varepsilon = 450$) and at 13,300 cm^{-1} ($\varepsilon = 210$),[3] attributable to the electronic transitions $d_{x^2-y^2}$, $d_{xy} \rightarrow d_{z^2}$, and d_{xz}, $d_{yz} \rightarrow d_{z^2}$.[16] This complex, therefore, must be formulated as $[CuBr(TSN)]Br$ with five-coordinated copper. Although five-coordinated copper complexes are rather common, this is one of the first examples where the ligands present contain thioethereal sulfur.[17]

The blue shift of the two bands in the TSN copper complex with respect to those of the Me$_6$tren analog, does not agree with the spectrochemical expectation. This fact may be explained by recalling that the geometry of the chelate rings in the $[CuBr(Me_6tren)]Br$ complex requires that the copper atom lies below the plane of the three basal nitrogens. With the ligand TSN, on the other hand, the larger radius of sulfur with respect to that of nitrogen would allow the copper atom to be closer to the plane of the three sulfur atoms. This makes the d_{z^2} and ($d_{x^2-y^2}$, d_{xy}) orbitals more σ-antibonding and the (d_{xz}, d_{yz}) orbitals less σ-antibonding in the TSN complex than in the Me$_6$tren complex, thus increasing the frequencies of the spectral transitions. Back donation from copper(II) to empty 3d sulfur orbitals, if present, could also give the same effect.

Finally, the 1:1 complex of zinc iodide with TSN is monomeric and essentially non conducting in 1,2-dichloroethane. This complex, therefore, must be formulated as $ZnI_2(TSN)$. Its stereochemistry is possibly octahedral but a lower coordination number cannot be safely ruled out. This could occur if one or two sulfur atoms were not bound. In nitroethane the compound exhibits a slight conductivity which is

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(11) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960); A. Turco and C. Pecile, *Nature*, *191*, 66 (1961); A. Sabatini and I. Bertini, *Inorg. Chem.*, *4*, 959 (1965).

(12) K. Nakamoto, «Infrared Spectra of Inorganic and Coordination Compounds», John Wiley and Sons, Inc., New York, N. Y., p. 175 (1963); D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, *4*, 715 (1965).

(13) C. K. Jørgensen, *Acta Chem. Scand.*, *10*, 887 (1956).

(14) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, *24*, 157 (1962).

(15) S. E. Livingstone, *Quart. Rev.*, (London), *19*, 386 (1965).

(16) M. Ciampolini and N. Nardi, *Inorg. Chem.*, *5*, 1150 (1966).

(17) *Cf. P. S.* Chia and S. E. Livingstone, *Austr. J. Chem.*, *21*, 339 (1968).

about 20% of that exhibited by typical 1:1 electrolytes under the same conditions. With respect to 1,2-dichloroethane, the partial displacement of iodide from the zinc coordination sphere in nitroethane, could be favored by the higher dielectric constant and/or by the higher solvating power of that solvent.

In conclusion, the ligand TSN forms complexes with some 3d metal ions which exhibit various stoichiometries and stereochemistries. Besides zinc, for which the actual coordination number with this ligand is not known, five-coordinated structures occur with copper(II) and cobalt(II) and octahedral structures occur with nickel(II). As an explanation of these facts it may be recalled that a calorimetric study[18] showed that the tendency of these three metal ions towards five-coordination as opposed to six-coordination decreases in the order: Cu>Co>Ni. It appears, therefore, that the ligand TSN is capable to discriminate among the theree metal ions giving five-coordinated complexes with copper and cobalt only and not with nickel. In this respect, TSN behaves as the less bulky ligand tren[5,19] and not as the bulkier ligand Me$_6$tren.[3,10] The latter ligand gives five-coordinated complexes even with nickel.

Apparently, other factors, besides crowding around the metal, are present as is shown by the fact that the only five-coordinated complexes of cobalt with TSN so far isolated have the structure [CoX(TSN)]$_2$-[CoX$_4$]. Such a structure is stabilized by a crystal lattice contribution which is greater than that for the 1:1 complexes [MX(ligand)]X. The failure to obtain cobalt complexes of the type [CoX(TSN)]X may perhaps be attributed to the weaker cobalt-thioethereal sulfur bond as compared with the cobalt-amine nitrogen bond.[20]

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(19) M. Ciampolini and P. Paoletti, *Inorg. Chem.*, 6, 1261 (1967); P. C. Jain and E. C. Lingafelter, *J. Am. Chem. Soc.*, 89, 724 (1967).

(20) C. K. Jørgensen, in «Inorganic Complexes», Academic Press, London, New York, pp. 131 ff. (1963).