CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E INORGANICA,
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# Five-Coordinated Complexes of the Transition Elements from Manganese to Zinc with Bis(2-dimethylaminoethyl)methylamine

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The tridentate ligand bis(2-dimethylaminoethyl)methylamine (dienMe) forms complexes with the bivalent transition ions from manganese to zinc having the general formula [M(dienMe)$X_2$] (where X = Cl, Br, I). Analytical, spectral, conductivity, and molecular weight data indicate that the metal is five-coordinated in these compounds. In chloroform solution a slight proportion of associated species is also present. The complexes from manganese to copper are all of the high-spin type. The [Fe(dienMe)$Cl_2$] complex is the first example of a high-spin complex of five-coordinated iron(II) so far described. The reflectance spectrum of the complex Co(dien)$Cl_2$ (dien = bis(2-aminoethyl)amine) supports the formulation [Co(dien)$_2$]-[$CoCl_4$] with both octahedral and tetrahedral cobalt(II), respectively.

## Introduction

Previous papers from this laboratory have reported the preparation and properties of high-spin five-coordinated complexes of 3d bivalent ions.[1-5] The complexes of manganese, cobalt, and nickel were the first examples of high-spin five-coordinated compounds.

We have now undertaken the study of compounds of the bivalent ions from manganese to zinc with the potentially tridentate ligand bis(2-dimethylaminoethyl)methylamine, $CH_3N[CH_2CH_2N(CH_3)_2]_2$. This triamine, which is a pentamethyl derivative of bis(2-aminoethyl)amine (dien), $NH(CH_2CH_2NH_2)_2$, is hereafter abbreviated dienMe. This paper reports the preparation and properties of complexes with the general formula M(dienMe)$X_2$ (where M = Mn, Fe, Co, Ni, Cu, and Zn; X = halogen).

TABLE I

PROPERTIES AND ANALYSES OF THE M(II) COMPLEXES

| Complex[a] | Color | Molar conductance, cm.$^2$/ohm $M^{b,c}$ Nitroethane | $i^d$ | | N, % | | Metal, % | | Halogen, % | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $CHCl_3$ | $C_2H_5NO_2$ | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| Mn(dienMe)$Cl_2$ | White | 2.0 | ... | 0.96 | 14.03 | 14.22 | 18.36 | 17.35 | 23.70 | 23.48 |
| Mn(dienMe)$Br_2$ | Buff | 5.8 | ... | ... | 10.82 | 10.40 | | | 41.18 | 41.09 |
| Fe(dienMe)$Cl_2$ | Amethyst | ... | ... | ... | 14.01 | 14.28 | 18.61 | 18.81 | 23.63 | 23.56 |
| Co(dienMe)$Cl_2$ | Violet | 1.1 | 1.11 | 0.97 | 13.86 | 13.97 | 19.44 | 19.48 | 23.39 | 23.27 |
| Co(dienMe)$Br_2$ | Violet | 2.7 | 1.15 | 0.96 | 10.74 | 10.91 | 15.09 | 14.85 | 40.87 | 40.45 |
| Co(dienMe)$I_2$ | Deep blue | 9.9 | ... | ... | 8.64 | 8.51 | 12.13 | 12.06 | 52.22 | 52.20 |
| Ni(dienMe)$Cl_2$[a] | Ochre | 2.0 | 1.14 | 0.92 | 13.89 | 13.93 | 19.38 | 19.35 | 23.40 | 23.35 |
| Ni(dienMe)$Br_2$ | Ochre | 4.9 | 1.25 | 0.87 | 10.72 | 10.42 | 14.97 | 14.95 | 40.79 | 40.40 |
| Ni(dienMe)$I_2$ | Red brown | 21.8 | ... | ... | 8.64 | 8.68 | 12.08 | 11.89 | 52.24 | 52.10 |
| Cu(dienMe)$Cl_2$ | Light blue | 16.1[c] | 1.30 | 0.78 | 13.65 | 13.60 | 20.65 | 20.56 | 23.04 | 22.89 |
| Cu(dienMe)$Br_2$ | Bright green | ... | ... | ... | 10.59 | 10.66 | | | 40.29 | 40.00 |
| Zn(dienMe)$Cl_2$ | White | 3.3 | 1.10 | 0.97 | 13.57 | 13.75 | 21.12 | 21.08 | 22.90 | 22.51 |
| Zn(dienMe)$Br_2$ | White | 4.1 | ... | 1.01 | 10.54 | 10.62 | 16.40 | 16.51 | 40.10 | 39.79 |

[a] Calcd.: C, 35.68; H, 7.65. Found: C, 36.08; H, 7.76. [b] For *ca.* $10^{-3}$ $M$ solutions at 25°. [c] The molar conductance in $10^{-3}$ $M$ solution in chloroform at 25° is 0.061; the molar conductance of [$(C_4H_9)_4N$]Br, is 0.260 under the same conditions. [d] van't Hoff coefficients for *ca.* $3 \times 10^{-2}$ $M$ solutions at 37°.

## Experimental Section

**General Preparation of Complexes.**—Hot solutions of the appropriate metal salt (0.010 mole) in 1-butanol (20 ml.) and bis(2-dimethylaminoethyl)methylamine[6] (0.011 mole) in 1-butanol (10 ml.) were mixed. Concentration by distillation followed by cooling yielded the required complex compound. The crystalline compounds were filtered in a closed system and dried in a moisture-free nitrogen stream. They were recrystallized from chloroform–petroleum ether mixtures. The manganese, iron, and cobalt compounds were prepared, filtered, and recrystallized in a pure nitrogen atmosphere.

**Materials and Measurements.**—The purification of the solvents as well as the apparatus and procedures used for the spectral, conductivity, magnetic, and molecular weight measurements are described in a previous paper.[1]

## Results

The analytical data and characteristics of the complexes of dienMe with halides of the transition elements from Mn to Zn are given in Table I. Though the

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(1) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).

(2) L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Am. Chem. Soc.*, **87**, 3102 (1965).

(3) P. L. Orioli, M. Di Vaira, and L. Sacconi, *Chem. Commun.* (London), 103 (1965).

(4) L. Sacconi, M. Ciampolini, and G. P. Speroni, *Inorg. Chem.*, **4**, 1116 (1965).

(5) L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965); L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965).

(6) A. Marxer and K. Miescher, *Helv. Chim. Acta*, **34**, 924 (1951).

compounds are hygroscopic, those of manganese, iron, and cobalt are stable in a desiccator for at least several months. The cobalt complex does not oxidize appreciably in solution, provided that the solvents are anhydrous.

The magnetic susceptibility of the compounds in solution and solid state has been measured (Table II).

Table II

Magnetic Data for Some M(dienMe)$X_2$ Complexes

| Compound | State | T, °C. | $\chi_g \times 10^6$ | $\chi_{Me} \times 10^6$ | $\mu_{eff}$, B.M. |
|---|---|---|---|---|---|
| Mn(dienMe)$Cl_2$ | Solid | 22 | 47.64 | 14,433 | 5.85 |
| Fe(dienMe)$Cl_2$ | Solid | 21 | 37.96 | 11,390 | 5.20 |
| Co(dienMe)$Cl_2$ | Solid | 18 | 28.82 | 8919 | 4.60 |
| Co(dienMe)$Br_2$ | $CHCl_3$ | 25 | 23.97 | 9595 | 4.80 |
| Ni(dienMe)$Cl_2$ | Solid | 19 | 15.43 | 4856 | 3.38 |
|  | $CHCl_3$ | 19 | 15.33 | 4826 | 3.38 |
| Ni(dienMe)$Br_2$ | $CHCl_3$ | 25 | 11.59 | 4744 | 3.38 |
| Cu(dienMe)$Cl_2$ | Solid | 20 | 4.06 | 1430 | 1.84 |
|  | $CHCl_3$ | 25 | 4.19 | 1471 | 1.88 |

The complexes from manganese to copper are all high-spin. In each case the magnitude of the orbital contribution to the magnetic moment is rather small. The magnetic moments of the nickel compounds are slightly higher than those usually found in octahedral complexes. The magnetic moments of the compounds in chloroform solution are practically identical with those in the solid state.

All these complexes, with the exception of copper, are nonconductors in chloroform and in nitrobenzene. This indicates that the halogen ions are coordinated to the metal. In solution in nitroethane these compounds show a slight conductivity, 2–9 $ohm^{-1}$ $mole^{-1}$ $cm.^2$ in $10^{-3}$ $M$ solution at 25°. These values are less than 10% of those obtained for 1:1 electrolytes, which is 90–100 $ohm^{-1}$ $mole^{-1}$ $cm.^2$ under the same conditions (Table I). This slight conductivity may be attributed to the partial displacement of a halogen in these compounds by the solvent. The copper complex shows appreciable conductance in chloroform and in nitrobenzene. The values of conductivity are also in this case a small fraction (≈20%) of those of the 1:1 electrolytes.

In chloroform the values of the molecular weight of the chloro compounds of the elements from cobalt to zinc, which are not oxidized, are about 10% (for copper 30%) greater than that calculated for a monomeric formula (Table I). This indicates the presence in this solvent of a small fraction of associated species. For the bromo complex of nickel, also in chloroform, this fraction increases to 25%. In nitroethane the values of the molecular weights are slightly less than those calculated for the monomeric formula. This is in accordance with the slight dissociation of halogen in this solvent, as the lower values of the apparent molecular weight correspond to the complexes with greater conductance (Table I).

The results of the measurements of molecular weight and conductivity lead to the conclusion that all these complexes are present in solution predominantly as nonionic monomeric species. Thus these will be formulated as [M(dienMe)$X_2$].

Table III

The Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes

| Compound | State | Absorption max., $cm.^{-1}$ ($\epsilon_{molar}$ for soln.) |
|---|---|---|
| Mn(dienMe)$Cl_2$ | Solid | 23,000, 27,000 |
| Fe(dienMe)$Cl_2$ | Solid | ≈4000, 8400 |
|  | $CHCl_3$ | <5000, 8600 (6) |
| Co(dienMe)$Cl_2$ | Solid | ≈4000, 8800, 10,500, 16,200, 19,000 |
|  | $CHCl_3$ | 8700 sh, 10,600 (19), 16,100 (106), 18,800 (112) |
| Co(dienMe)$Br_2$ | Solid | ≈4000, 8200, 10,400, 15,800, 18,900 |
|  | $CHCl_3$ | 8600 (19), 10,300 (20), 15,800 (158), 18,500 (122) |
| Co(dienMe)$I_2$ | Solid | ≈4000, 8100, 10,200, 15,700, 18,500 |
|  | $CHCl_3$ | 8000 (27), 10,000 (22), 15,400 (225), 18,100 (141), 20,400 sh, 26,300 sh |
| Ni(dienMe)$Cl_2$ | Solid | ≈5000, 9600 sh, 12,700, 15,700 sh, 18,900 sh, 21,700 |
|  | $CHCl_3$ | <5000, 9600 sh, 11,400 sh, 12,700 (42), 15,900 sh, 18,700 sh, 21,500 (165) |
| Ni(dienMe)$Br_2$ | Solid | ≈5000, 9800 sh, 11,100 sh, 12,500, 15,400 sh, 18,200 sh, 21,600 |
|  | $CHCl_3$ | <5000, 7100 sh, 8700 sh, 11,000 sh, 12,500 (46), 15,500 sh, 18,200 sh, 21,400 (188), 27,800 (445) |
| Ni(dienMe)$I_2$ | Solid | ≈5000, 7200, 12,200, 14,300 sh, 21,200 |
| Cu(dienMe)$Cl_2$ | Solid | 13,100 |
|  | $CHCl_3$ | 12,700 (259) |
|  | $C_2H_5NO_2$ | 12,500 (236), 21,100 (62) |
| Cu(dienMe)$Br_2$ | Solid | 13,000 |

The spectra of these compounds have been measured both in the solid state and in solution. Band maxima and molar absorbancies are reported in Table III. For the chloro complexes from iron to copper the reflectance spectra of the solid state are shown in Figure 1. The spectra of the solids are not significantly different from those of the solutions in chloroform and nitrobenzene. Substantially the same applies to the spectra in nitroethane with the exception of that of copper, which presents a band at 21,000 $cm.^{-1}$, which is absent in the solid and in chloroform solution. In methanol, ethanol, and water there are, however, marked shifts in the frequencies of the peaks and variations of the molar absorbance. These facts are clearly indicative of extensive solvation.

The spectra of the solid chloro, bromo, and iodo complexes of a given element are very similar to each other, as they only show slight displacements of the frequencies of the peaks, which can be well correlated with the positions of the halogen in the spectrochemical series. Accordingly these halides of a given element must be strictly stereochemically similar.

X-Ray powder photographs have been taken on chloro and bromo complexes. Those of the bromo complexes studied here, that is, of Mn, Co, Ni, Cu, and Zn, are practically indistinguishable. The chloro complexes show, however, two types of photographs: one type is presented by the compounds of manganese, iron, cobalt, and zinc; the other type, by the compounds of nickel and copper.

## Discussion

All the solid compounds have essentially the same stereochemistry. This is not only evident for the bromo compounds, which are all isomorphous; but is also clear for the chloro and iodo derivatives, because of the strong similarity of these spectra with those of the bromo complexes. In particular for the chloro complexes the differences found in the powder photographs can probably be attributed to differences in the packing of the molecules in the crystal lattice rather than to substantial differences in the stereochemistry of the compounds.

The similarity of the spectra of the complexes from iron to copper in the solid state and in solution indicates that the same stereochemistry is maintained in the species which predominate in solution. These, as can be seen in the preceding section, must be formulated as [M(dienMe)$X_2$]. As the ligand dienMe is potentially tridentate, the coordination number of the metal in this species cannot be more than five. The spectral and magnetic data for the compounds from iron to copper are throughly in accord with a five-coordinated high-spin structure. On the other hand they cannot be consistently interpreted in terms of a tetrahedral (distorted) structure, which might appear if a nitrogen atom was not coordinated.[7]

Specifically, the crystal field spectra of these dienMe complexes in the range from 4000–30,000 cm.$^{-1}$ are similar to those of high-spin compounds, to which the five-coordinated structure (distorted trigonal-bipyramidal) has been attributed or verified by X-ray crystallography. These are $[(CH_3NCH{\cdot}C_6H_4O)_2M]_2$ (M = Co(II),[2,3] Ni(II),[2] Cu(II)[2]) and [M(trenMe)X]X[1] (M = Fe, Co, Ni, Cu; X = Cl, Br, I, $ClO_4$, $NO_3$; trenMe = $N[CH_2CH_2N(CH_3)_2]_3$). Compared with the spectra of these last compounds which contain donor atom sets, $N_2O_3$ or $N_4X$, respectively (X = Cl, Br, I, O), a displacement of the frequencies of the peaks toward the red is generally noticeable. This is to be expected because the donor set, in this case, is $N_3X_2$ (X = halogen).

Thus the Fe(dienMe)$Cl_2$ complex shows a spin-allowed band at 8500 cm.$^{-1}$ ($\epsilon \approx 6$) to be correlated with the band at 10,000 cm.$^{-1}$ from [Fe(trenMe)Cl]Cl.[8] An absorption band also appears around 4000 cm.$^{-1}$, but determination of its exact location is interfered with by ligand overtones.

For the Co(dienMe)$Cl_2$ complex the bands at 5500, 10,600, 16,200, and 18,800 cm.$^{-1}$ can be correlated with the bands from the [Co(trenMe)Cl]Cl complex at 5800, 12,700, 15,600–16,200, and 20,200 cm.$^{-1}$. The frequencies of the first and of the third of these bands are practically the same for the two compounds, confirming the previously observed weak sensitivity of these bands to the intensity of the crystal field.[1] One finds similar behavior for the bromo and iodo complexes.

For the Ni–dienMe compounds, all the bands are displaced 1500–2000 cm.$^{-1}$ toward lower frequencies compared with those of the corresponding compounds Ni–trenMe.

For Cu(dienMe)$Cl_2$ there is a broad asymmetric band (Figure 1) with its maximum at about 13,000 cm.$^{-1}$ and with a tail toward the red, which reveals at least two transitions in its envelope. Two incompletely resolved bands are also present (in the same region) in the spectrum of bis(N-methylsalicylaldiminato)copper(II),[2] which has a trigonal-bipyramidal structure. This structure occurs when this complex is included in the lattice of the analogous zinc complex.[2] The compound [Cu(trenMe)Br]Br shows the two resolved bands.[1] Meek and Ehrhardt have studied copper(II) complexes with analogous N,N′-substituted ethylenediamine ligands.[9] They have shown that the complexes with a square-planar structure have a complex broad band, at higher frequencies (15,000–20,000 cm.$^{-1}$), while the octahedral complexes have a diffuse band at 13,000–18,000 cm.$^{-1}$ and a band at 21,000–23,000 cm.$^{-1}$. In solution the Cu(dienMe)$Cl_2$ complex in nitroethane also shows a weaker band at 21,000 cm.$^{-1}$ as well as the band at 13,000 cm.$^{-1}$. This band may be attributed to the presence of octahedral species, probably through solvation. On the other hand, the absence of this band in spectra in chloroform solution seems to indicate that the polymeric forms present in this solvent are not octahedral. It is interesting to note that Meek and Ehrhardt[9] exclude both a planar and an octahedral structure for the compound $Cu[(CH_3)_2NCH_2CH_2NHCH_3]_2Br_2$ because of the form of its spectrum. However, such a spectrum[9] appears to be very similar to that of Cu(dienMe)$Br_2$ and it is therefore likely that a five-coordinated structure may also be attributed to the former compound. This is also in accordance with the value of the conductivity in nitromethane, reported by Meek and Ehrhardt, which is typical of 1:1 electrolytes.[9]

All the above-mentioned evidence leads us consistently to assign a pentacoordinate structure to the complexes in the solid state studied here. For the complexes with iron, cobalt, nickel, and copper this pentacoordinated structure is also maintained in the species predominant in solutions, as is shown by the similarity of the spectra of the solids and the solutions. For the complexes of manganese and zinc, where the spectral criterium fails, there is no proof that the species predominantly present in solution are not also five-coordinate, as they are in the solid state.

In the absence of a direct X-ray structure determination, the actual stereochemical arrangement of the five-coordinating atoms is not sure.[10] The non-

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[7] In effect only the tetrahedral structure is to be considered because the planar complexes of iron, cobalt, and nickel with a similar set of donor atoms have always been found to be of low spin.

[8] Unpublished results of this laboratory.

[9] D. W. Meek and S. A. Ehrhardt, *Inorg. Chem.*, **4**, 584 (1965).

[10] A tridimensional X-ray analysis of the Co(dienMe)$Cl_2$ compound is now in progress in this laboratory by Drs. M. Di Vaira and P. L. Orioli. At the present stage of the investigation the discrepancy factor is 15%. The structure consists of discrete molecules in which cobalt has just a coordination number of five.

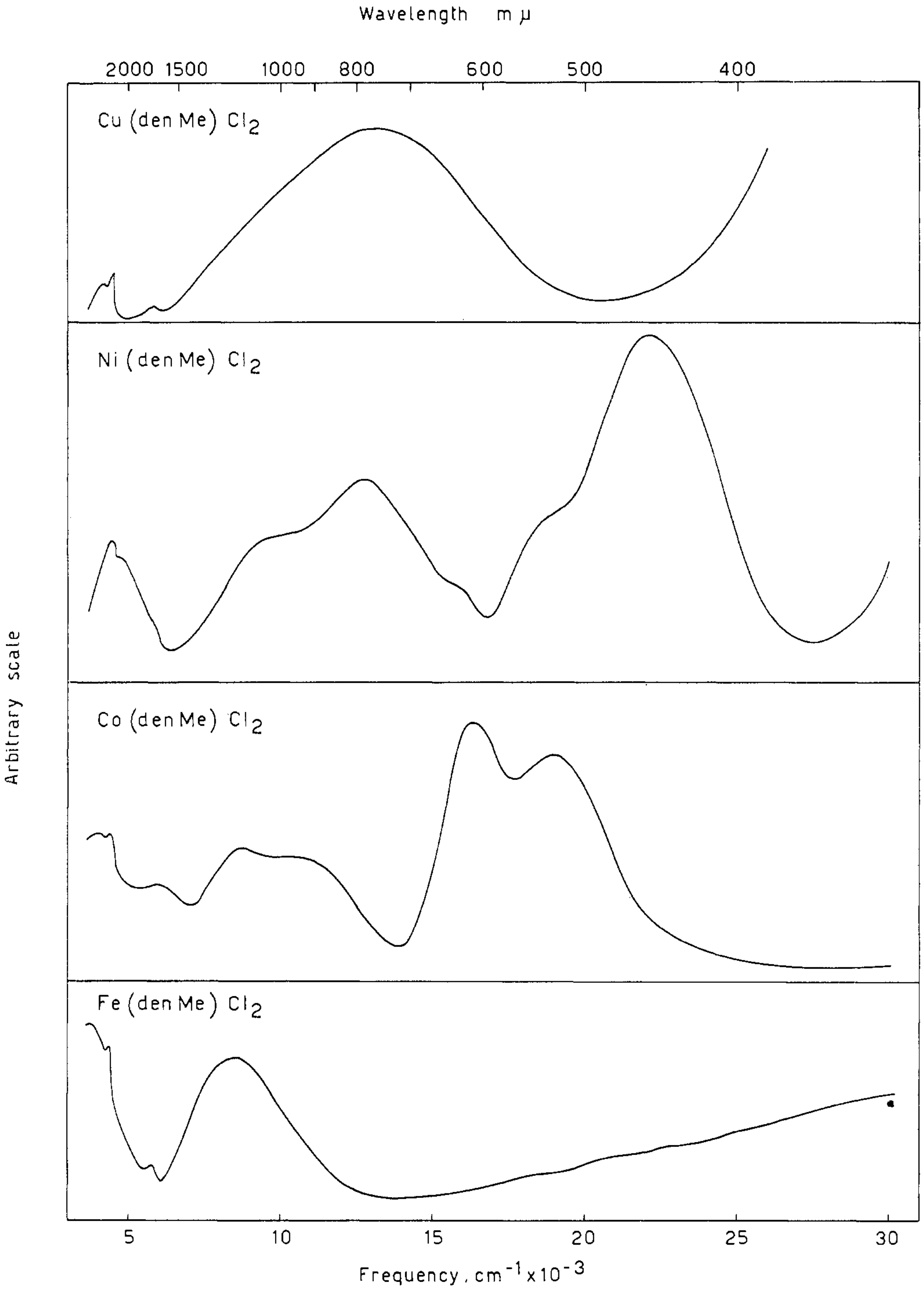

Figure 1.—Reflectance spectra of some M(dienMe)$Cl_2$ complexes.

equivalence of the donor atoms and the geometry of the organic ligand, which imposes that the N–M–N angle of the chelate ring is $\leq 90°$, are such that the structure of these complexes can be neither strictly a trigonal bipyramid nor a square pyramid. Perhaps an intermediate structure between these two stereochemical extremes is the one that actually occurs.

In conclusion the compounds of this series join the few examples of high-spin five-coordinated complexes. The compound Fe(dienMe)$Cl_2$ is the first example of a five-coordinated high-spin iron(II) compound.[11] It is interesting to remember that the cobalt(II) and nickel(II) complexes with ligands structurally similar but containing As or P in place of N, *e.g.*, $CH_3As[CH_2CH_2CH_2As(CH_3)_2]_2$,[12] are all low-spin.[12,13] This is probably the result of the fact that the coordinated bonds are more covalent in character with donor atoms like P and As than with N. In fact the electronegativity of the first two elements is very near to that of these metal ions. π bonding may also play a part in promoting

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[11] *Cf.* A. F. Wells in "Structural Inorganic Chemistry," Oxford University Press, London, 1962, p. 918; S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

[12] R. S. Nyholm, *Chem. Rev.*, **53**, 263 (1953); G. A. Barclay and R. S. Nyholm, *Chem. Ind.* (London), 378 (1953); G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1960).

[13] G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1955), and previous references therein.

spin pairing, although in the case of nickel it does not seem to occur extensively.[13]

With the nonmethylated $NH(CH_2CH_2NH_2)_2$ (dien) ligand all the ions from $Mn^{2+}$ to $Zn^{2+}$ form complexes of the type $M(dien)^{2+}$ and $M(dien)_2^{2+}$ in aqueous solution.[14,15]

With the possible exception of the compounds of copper and zinc the others are all octahedral (the first ones through coordination of three molecules of water).[15] Moreover, Bernhard and Barclay isolated the compounds $Co(dien)Cl_2$ and $Co(dien)Br_2$ which are high-spin.[16] For these compounds they postulate a structure either of the type $[Co(dien)X]X$ (with cobalt pseudotetrahedral) or of the type $[Co(dien)_2][CoX_4]$ (with tetrahedrally and octahedrally coordinated cobalt present at the same time).[16] We have now measured the reflectance spectrum of the $Co(dien)Cl_2$ compound, between 5000 and 30,000 cm.$^{-1}$. It shows intense bands in the regions 5000–6000 and 14,000–20,000 cm.$^{-1}$ diagnostic of the $(CoCl_4)^{2-}$ species and one weaker band at 10,500 cm.$^{-1}$ characteristic of the hexamine cobalt(II) species. These data lead to the conclusion that the structure is $[Co(dien)_2][CoX_4]$. Thus it appears clear that a structure which contains six- and four-coordinated cobalt present at the same time is more stable than one with a five-coordinated cobalt when the ligand is dien. The opposite is true when the ligand is dienMe. It is very likely that this is due to the steric requirements of the methyl groups of the ligand dienMe, which cause strong steric hindrance to the coordination of two dienMe molecules to the same metal ion. In fact Stuart models of the ion $[M(dienMe)_2]^{2+}$ cannot be assembled. One must not, however, exclude the fact that a high contribution of lattice energy contributes to the stability of the ionic structure $[Co(dien)_2]$-$[CoX_4]$. Unfortunately the insolubility of these compounds in inert solvents prevents us from ascertaining if this structure is also maintained in the absence of crystal forces.[17]

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(14) J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 985 (1950).

(15) M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 2994 (1961), and previous reference therein.

(16) G. A. Barclay and A. K. Bernard, *ibid.*, 2540 (1958).

(17) NOTE ADDED IN PROOF.—Professor R. S. Nyholm and his co-workers have recently reported [*Nature*, **207**, 72 (1965)] the isolation of high-spin five-coordinated complexes of bivalent transition metals from manganese to zinc (diamagnetic). X-Ray data indicate [P. Pauling, G. B. Robertson, and G. A. Rodley, *ibid.*, **207**, 73 (1965)] that these compounds have a square-pyramidal configuration.

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# Coordination Compounds of Thallium(III). II. Some Complexes of Thallium(III) Halides and Their Indium(III) Analogs

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The preparation and characterization of some new complexes of indium(III) and thallium(III) halides are described. Generally, complexes of the types $InCl_3 \cdot 3L$ and $TlX_3 \cdot 2L$ were obtained, although reaction of indium(III) chloride with 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy) in methyl cyanide gave the complexes $InCl_3 \cdot 1.5phen \cdot CH_3CN$ and $InCl_3 \cdot 1.5bipy$, respectively. Conductivity and far-infrared spectral data of the complexes have been used as a guide to their stereochemistry.

## Introduction

At present little information is available on the stereochemistry of thallium(III) complexes, and previous studies have been mainly concerned with the preparation and stoichiometry of such complexes. However, conductivity and molecular weight measurements have recently[1–3] been carried out on some complexes of the thallium(III) halides and the tetrahalothallate ions $TlX_4^-$, where X = Cl, Br, or I. A tetrahedral structure has been definitely established for $TlCl_4^-$ in $(C_6H_5)_4AsTlCl_4$,[1] while both tetrahedral[4] and square-planar[5] crystal structures for $TlBr_4^-$ have been claimed.

As an extension to our earlier studies[1] on complexes of the thallium(III) halides, we have now prepared some further adducts of the type $TlX_3 \cdot 2L$ and their corresponding indium(III) chloride complexes $InCl_3 \cdot 3L$. Conductivity and infrared studies on these and other complexes described previously[1] are now reported.

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(1) F. A. Cotton, B. F. G. Johnson, and R. M. Wing, *Inorg. Chem.*, **4**, 502 (1965).

(2) (a) F. Ya. Kul'ba, V. E. Mironov, C. Ta'ung, and Z. G. Filippova, *Zh. Neorgan. Khim.*, **8**, 672 (1962); (b) F. Ya. Kul'ba, V. E. Mironov, V. I. Sazhina, and T. G. Ogibenina, *ibid.*, **7**, 911 (1963).

(3) (a) G. J. Sutton, *Australian J. Chem.*, **11**, 120 (1958); (b) G. J. Sutton, *ibid.*, **16**, 1134 (1963).

(4) A. C. Hazell, *J. Chem. Soc.*, 3459 (1963).

(5) T. Watanabe, Y. Sarto, R. Shino, and M. Atoji, *Struct. Rept.*, **11**, 393 (1947–1948).