predominates for chloride entry, but, when the electrophilic contribution reaches its maximum, the rate starts to decrease as the strength of the bond between the metal and the leaving group increases. These effects can also be observed in the reaction with azide but they are less marked.

## Experimental Section

Trichloropyridinegold(III) and trichloroquinolinegold(III) were first characterized by Renz,[17] but the other complexes are described here for the first time. All of the complexes were prepared by the following general method. Equimolar amounts of the appropriate organic heterocyclic base were added to a concentrated aqueous solution of chloroauric acid which had previously been carefully neutralized with sodium carbonate. A yellow precipitate formed almost immediately and was filtered off and washed repeatedly with water and methanol and then dried over phosphorus pentoxide under vacuum. The precipitate could be recrystallized from anhydrous methanol, but this led to considerable loss of yield and to further decomposition, and it was found to be preferable, for the kinetic studies, to use the original precipitate that had been washed repeatedly with water and methanol. The analyses are reported in Table II. Attempts to make analogous complexes with piperidine, toluidine, and naphthylamine resulted in the reduction of the complex to metallic gold.

Anhydrous lithium chloride was recrystallized repeatedly from acetone and dried and stored in a vacuum desiccator. Sodium nitrite and sodium azide (AR grade) were recrystallized repeatedly from methanol and dried and stored in the dark in a vacuum desiccator.

AnalaR methanol was used without further treatment since small traces of water did not appear to have any effect upon the reactions.

**Kinetics.**—Methanolic solutions of the complex (generally in the range $10^{-5}$–$10^{-4}$ $M$) and the appropriate reagent ($10^{-5}$–$10^{-2}$ $M$) were prepared and stored separately in a thermostat. The reaction was started by mixing known volumes of the two solutions in the spectrophotometer cell, which was then placed in the thermostated compartment of the spectrophotometer. Most of the measurements were made with a Unicam SP 800 double-beam recording spectrophotometer. The slower reactions were followed by scanning the near-ultraviolet spectrum from time to time in the course of the reaction. In this way it was possible to separate and identify the individual stages of the reaction and then collect the appropriate optical density data. When the reaction was so fast that the time taken to scan an individual spectrum was a significant part of the time of the over-all reaction, the measurements were made at a single wavelength chosen after preliminary scanning experiments. The results were either recorded by allowing the chart to move at a known rate while the spectrophotometer was locked at the chosen wavelength or else obtained manually using a Unicam SP 500 spectrophotometer.

Table II

Analytical Data for the Complexes of the Type $[AuCl_3am]^0$

| am | Complex | C, % Calcd | C, % Found | H, % Calcd | H, % Found | Cl, % Calcd | Cl, % Found |
|---|---|---|---|---|---|---|---|
| Pyridine | $C_5H_5NCl_3Au$ | 15.7 | 16.3 | 1.3 | 1.4 | 27.8 | 27.5 |
| Quinoline | $C_9H_9NCl_3Au$ | 24.7 | 24.9 | 1.6 | 1.7 | 24.4 | 24.4 |
| Isoquinoline | $C_9H_9NCl_3Au$ | 24.7 | 25.0 | 1.6 | 1.8 | 24.4 | 23.7 |
| 4-Methylpyridine | $C_6H_7NCl_3Au$ | 18.2 | 18.3 | 1.7 | 1.9 | 26.8 | 27.2 |
| 3-Methylpyridine | $C_6H_7NCl_3Au$ | 18.2 | 18.6 | 1.7 | 1.8 | 26.8 | 26.5 |
| 3,5-Dimethylpyridine | $C_7H_9NCl_3Au$ | 20.5 | 20.5 | 2.2 | 2.2 | 25.9 | 25.4 |
| 2,6-Dimethylpyridine | $C_7H_9NCl_3Au$ | 20.5 | 21.3 | 2.2 | 2.3 | 25.9 | 25.9 |

**Acknowledgments.**—L. C. wishes to thank the Italian Council for Research (C.N.R., Rome) for a fellowship and the Institute of General Chemistry of the University of Padua for a leave of absence.

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[17] C. Renz, *Z. Anorg. Chem.*, **36**, 100 (1903).

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Contribution from the Istituto di Chimica Generale e Inorganica,
Università di Firenze, Florence, Italy

# Trigonal Bipyramidal Complexes of Bivalent Manganese, Iron, and Zinc with Tris(2-dimethylaminoethyl)amine

By M. CIAMPOLINI and N. NARDI

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The quadridentate ligand tris(2-dimethylaminoethyl)amine ($Me_6tren$) forms 1:1 complexes with $MnBr_2$, $MnI_2$, $FeBr_2$, $ZnBr_2$, and $ZnI_2$. X-Ray powder photographs and conductivity and spectral data indicate that these complexes must be formulated as $[M(Me_6tren)X]X$. The metal is five-coordinated with an approximately trigonal bipyramidal configuration. Manganous and ferrous compounds are of the high-spin type. A simple crystal field model is employed in order to calculate the splitting of the $^5D$ ground terms of the $d^4$ and $d^6$ configurations in $C_{3v}$ fields. The spectra of $[Fe(Me_6tren)Br]Br$ and of $[Cr(Me_6tren)Br]Br$ are discussed on this basis.

## Introduction

Five-coordinated complexes of elements of the first transition group are still rather rare. In particular, those of manganese(II)[1] and of iron(II)[2,3] have only recently been isolated.

In this laboratory five-coordinated complexes of bivalent ions of the first transition group with ligands capable of giving high-spin configurations are being investigated. Previous studies have shown that the quadridentate amine $N[CH_2CH_2N(CH_3)_2]_3$, tris(2-di-

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

[2] J. Lewis, R. S. Nyholm, and G. A. Rodley, *Nature*, **207**, 72 (1965).

[3] M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, **5**, 44 (1966).

TABLE I

SUMMARY OF PHYSICAL AND ANALYTICAL DATA FOR [M(Me$_6$tren)X] COMPLEXES

| Compd | Color | % N Calcd | % N Found | % metal Calcd | % metal Found | % halogen Calcd | % halogen Found | Molar conductance, cm$^2$/ohm-mole of nitroethane[a] |
|---|---|---|---|---|---|---|---|---|
| [Mn(Me$_6$tren)Br]Br | Greenish white | 12.59 | 12.48 | | | 35.90 | 35.86 | 93 |
| [Mn(Me$_6$tren)I]I | Green | 10.39 | 10.35 | | | 47.08 | 46.80 | 79 |
| [Fe(Me$_6$tren)Br]Br | White | 12.56 | 12.44 | 12.52 | 12.70 | 35.83 | 35.88 | 63 |
| [Zn(Me$_6$tren)Br]Br | White | 12.30 | 12.36 | | | 35.08 | 34.99 | 74 |
| [Zn(Me$_6$tren)I]I | White | 10.19 | 10.18 | 11.89 | 11.63 | 46.18 | 46.23 | 82 |

[a] For *ca.* $10^{-3}$ *M* solutions at 25°. Reference values in nitroethane are: [(*n*-$C_4H_9$)$_4$N]Br, 70, [(*n*-$C_4H_9$)$_4$N]I, 83.

methylaminoethyl)amine (Me$_6$tren),[4] forms high-spin five-coordinated complexes of the type [M(Me$_6$tren)X]X with M = Cr[5] and Co, Ni, Cu;[6] X = Cl, Br, I, $ClO_4$, $NO_3$. This paper describes the reaction between the Me$_6$tren ligand and manganese(II), iron(II), and zinc(II) halides. The compounds have been investigated by means of spectrophotometric, magnetic, and electric conductivity measurements and X-ray powder photographs, in order to elucidate their stereochemistry.

## Experimental Section

**Materials.**—All solvents were of reagent grade quality. Nitroethane and dichloromethane were washed with 5% aqueous sodium hydrogen carbonate, dried for 24 hr over anhydrous calcium chloride, and fractionally distilled.

**Synthesis of [N($CH_2CH_2NH_3$)$_3$]$Cl_3$.**—The preparation of N-[$CH_2CH_2N(CH_3)_2$]$_3$ from [N($CH_2CH_2NH_3$)$_3$]$Cl_3$ has been previously described.[6,7] The following preparation of [N($CH_2CH_2NH_3$)$_3$]$Cl_3$, however, has proved to be more profitable than that reported by Ristempart.[8] A suspension of 47 g (0.20 mole) of [NH($CH_2CH_2Cl$)$_2$]Cl,[9] 80 g of anhydrous potassium carbonate, and 120 g (0.66 mole) of potassium phthalimide in 300 ml of dimethylformamide was heated on a water bath for about 8 hr with occasional shaking. The mixture was then poured into water (2 l.). The sticky solid was separated by decantation and boiled with ethanol, and the resulting white powder was collected on a filter. This solid (80 g) was probably impure 2,2′,2″-triphthalimidotriethylamine (mp 182–185°, lit.[8] 187°) but it was not further characterized. On hydrolysis with ethanolic hydrazine,[10] it yielded [N($CH_2CH_2NH_3$)$_3$]$Cl_3$ (36 g, 0.14 mole). *Anal.* Calcd for [N($CH_2CH_2NH_3$)$_3$]$Cl_3$: Cl, 41.61. Found: Cl, 41.62.

**Preparation of the Metal Complexes.**—The complexes of Me$_6$tren with the metal halides were obtained by adding a solution of 3.0 g (*ca.* 0.013 mole) of the amine in 10 ml of butanol to a hot solution of 0.010 mole of the appropriate anhydrous halide in 20 ml of butanol. The gelatinous precipitate, which formed in some cases, redissolved after boiling for a few minutes. On cooling and slowly adding 20 ml of petroleum ether (bp 40–70°) tetrahedral crystals separated. The mother liquor was removed by decantation and the crystals washed with a 1:1 mixture of butanol–petroleum ether. Crystals were then filtered, washed with petroleum ether, and dried at 80° in a stream of dry nitrogen. In the case of oxidizable metals all of the operations were executed in an atmosphere of pure nitrogen. All of the complexes were recrystallized by dissolving them in chloroform containing a few drops of Me$_6$tren, and adding petroleum ether to the filtered solution.

TABLE II

MAGNETIC DATA FOR SOME [M(Me$_6$tren)X]X COMPLEXES IN THE SOLID STATE

| Compd | *t*, °C | $10^6\chi_g$ | $10^6\chi_{Me}$ | $\mu_{eff}$, BM |
|---|---|---|---|---|
| [Mn(Me$_6$tren)Br]Br | 20 | 33.95 | 15,375 | 6.01 |
| [Mn(Me$_6$tren)I]I | 18 | 27.54 | 15,133 | 5.95 |
| [Fe(Me$_6$tren)Br]Br | 20 | 23.89 | 12,022 | 5.34 |

**Physical Measurements.**—The conductivity values were measured on a WTW Model LBR/B conductance bridge. Concentrations of the solutions were approximately $10^{-3}$ *M*.

The apparatus and the experimental technique used for the magnetic measurements were described in a previous paper.[11] The Gouy tube was calibrated with freshly distilled water and nickel chloride solution.[12] Diamagnetic corrections were calculated from Pascal's constant.[13]

## Results

The chlorides of manganese(II) and zinc(II) do not give 1:1 complexes with Me$_6$tren in contrast to what was found with cobalt and nickel.[6] With $FeCl_2$ a 1:1 complex has been obtained once, but subsequent attempts have not been successful. Instead, homogeneous solids are formed, which have a metal:amine ratio greater than 1. These will be described elsewhere.

With bromides and iodides, however, very hygroscopic but well-formed tetrahedral crystals were obtained. The analytical and characteristic data of these manganese, iron, and zinc halides are given in Table I. All of the compounds are soluble in nitroethane, nitrobenzene, chloroform, dichloromethane, and alcohols, but they cannot be dissolved in nonpolar solvents. The manganese and iron compounds do not oxidize appreciably in dry air for some weeks. They are quickly oxidized, however, in damp air or in solution, even in anhydrous solvents.

The magnetic moments of the manganese and iron complexes (Table II) at room temperature are those typical of the high-spin configurations of each element.[14]

Spectra of the solid compounds and of their solutions in dichloromethane and nitroethane have been recorded. The absorption maxima and the molar ab-

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(4) In this paper the abbreviation Me$_6$tren is used, instead of the earlier trenMe (*cf.* ref 6), to accord with the abbreviation used by Professor Basolo for analogous ligands.

(5) M. Ciampolini, *Chem. Commun.*, 47 (1966).

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

(7) R. H. Mizzoni, M. A. Hennessey, and C. R. Scholz, *J. Am. Chem. Soc.*, **76**, 2414 (1954).

(8) E. Ristempart, *Ber.*, **20**, 2526 (1896).

(9) J. P. Mason and D. J. Gosch, *J. Am. Chem. Soc.*, **60**, 2816 (1938).

(10) P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963).

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

(12) B. N. Figgis and J. Lewis, *Mod. Coord. Chem.*, 415 (1960).

(13) B. N. Figgis and J. Lewis, *ibid.*, 403 (1960).

(14) P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1956, p 206 ff.

TABLE III
THE MAXIMA AND EXTINCTION COEFFICIENTS FOR THE ELECTRONIC SPECTRA OF THE COMPLEXES

| Compd | State | Absorption max, cm$^{-1}$ ($\epsilon_{\text{molar}}$ for soln) |
|---|---|---|
| [Mn(Me$_6$tren)Br]Br | Solid | 15,400, 21,150, 22,700, 24,900, 26,700 |
| | CH$_2$Cl$_2$ | 16,300 (0.4), 21,200 (1.0), 22,900 (1.0), 25,000 sh, 26,900 (1.2), 27,800 sh |
| [Mn(Me$_6$tren)I]I | Solid | 15,200, 21,200, 22,750, 24,800, 26,600 sh |
| | CH$_2$Cl$_2$ | 16,000 (2.1), 21,300 (4.8), 23,100 (4.8), 24,950 (7.5) |
| [Fe(Me$_6$tren)Br]Br | Solid | <4000, 9800, 14,300, 18,500, 19,250 sh, 21,300, 23,150, 24,700, 26,300 |
| | CH$_2$Cl$_2$ | <4000, 9800 (12.0), 14,400 (0.8), 16,150 sh, 18,600 (0.8), 19,350 sh, 21,300 (1.0), 23,150 (1.1), 24,900 (1.3), 26,200 (1.3) |

sorbancies are given in Table III. The appearance of the diffuse reflectance spectra of the solids closely resembles that of the complexes in solution. This indicates that there is no gross change in the stereochemistry of the manganese and iron complexes on dissolution. The electric conductivity of *ca.* $10^{-3}$ *M* solutions in nitroethane has been measured at 25° (Table I). The values are those typical of 1:1 electrolytes under the same conditions. The crystalline habit and X-ray powder photographs of the manganese, iron, and zinc halides are practically indistinguishable from those of the analogous cobalt, nickel, and copper compounds to which a five-coordinated trigonal bipyramidal structure has been attributed.[6]

## Discussion

The isomorphism of the bromides and iodides of manganese, iron, and zinc with those of cobalt, nickel, and copper confirms that the former complexes also have a five-coordinated structure in the solid state. A three-dimensional X-ray analysis, which is at present in progress[15] on the [Co(Me$_6$tren)Br]Br compound, has shown that the metal atom has a trigonal bipyramidal configuration with $C_3$ symmetry. The central nitrogen atom of the ligand and the coordinated bromine atom are on the threefold axis, and the three dimethylamine groups lie at the corners of an equilateral triangle. The metal atom lies slightly outside this triangle toward the coordinated bromine atom. The N–Co–N angle of each chelate ring—hereafter called $\beta$—is therefore slightly less than 90°, as often found in metal chelates of ethylenediamine and diethylenetriamine.[16] The similarity of the solid-solution spectra for manganese and iron and the character of 1:1 electrolytes indicate that this structure is also preserved in solution. These compounds must therefore be formulated as [M(Me$_6$tren)X]X.

While various five-coordinated complexes of zinc have been known for a long time,[17] those of manganese(II) and iron(II) are still rather rare. Only recently a description has appeared of a trigonal bipyramidal complex of manganese with N-methylsalicylaldimine[1] and of square-pyramidal complexes of manganese and iron with (CH$_3$)(C$_6$H$_5$)$_2$AsO and perchlorate anions.[2] Five-coordinated complexes of manganese and iron with a stereochemistry intermediate between the two forms mentioned above have also been prepared from the bis(2-dimethylaminoethyl)methylamine ligand and halides.[3] All of these five-coordinated complexes, which contain oxygen, nitrogen, and halogen as donor atoms, have high-spin configurations. With the quadridentate ligands P[*o*-C$_6$H$_4$P(C$_6$H$_5$)$_2$]$_3$ (QP) and As[*o*-C$_6$H$_4$As(C$_6$H$_5$)$_2$]$_3$ (QAS) and halides, however, Venanzi has obtained trigonal bipyramidal complexes of iron(II) with spin $S = 1$.[18,19] The spin pairing in the QP and QAS complexes seems to indicate a greater energy difference between the antibonding molecular orbitals of the type e′ and a$_1$′ [20] in the complexes with phosphorus and arsenic than in the complexes with nitrogen. This is very likely because the covalent character of the M–P and M–As bonds is greater than that of the M–N bond, as may be expected on the basis of electronegativity considerations.

The spectra of the manganese(II) and iron(II) complexes (Table III) are interesting because they are the first spectra to be reported for trigonal bipyramidal configurations with high-spin for these elements. Those of manganese show only weak bands above 15,000 cm$^{-1}$ ($\epsilon \approx 0.4$–1.2 for the bromide), which must be attributed to spin-forbidden transitions from the ground sextet state to the first excited quartet levels. The spectrum of the [Fe(Me$_6$tren)Br]Br complex shows bands of low intensity above 14,000 cm$^{-1}$ which must be attributed to spin-forbidden transitions from the ground quintet state to the first excited triplet states. Furthermore, in this spectrum there are two more intense bands at lower frequencies. One of them at 9800 cm$^{-1}$, has a molar absorbance of 12 at its peak (oscillator strength $P = 1.0 \times 10^{-4}$). The other band is in the region below 6000 cm$^{-1}$. In this region there is also absorption due to ligand harmonics, but a comparison with both the reflectance (Figure 1) and absorption spectra of the [Zn(Me$_6$tren)Br]Br compound shows clearly that there is a fairly intense band—not attributable to the ligand—which probably has its maximum below 4000 cm$^{-1}$. Such a region is, however, beyond the measuring limit of our spectrophotometer. Because of their intensity these two bands must be attributed to two spin-allowed transitions. A simple crystal field calculation (see Appendix) using the model of five-point dipoles shows, in fact, that two spin-allowed transitions may be expected

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(15) We wish to thank Drs. P. L. Orioli and M. Di Vaira for making available to us the results of the X-ray investigation prior to publication.

(16) *Cf.* B. Bruce and E. C. Lingafelter, *Acta Cryst.*, **17**, 254 (1964); F. A. Cotton and R. A. Elder, *Inorg. Chem.*, **3**, 397 (1964); M. Di Vaira and P. L. Orioli, *Chem. Commun.*, 590 (1965).

(17) *Cf.* P. L. Orioli, M. Di Vaira, and L. Sacconi, *Inorg. Chem.*, **5**, 400 (1966), for a review on the subject.

(18) L. M. Venanzi, *Angew. Chem. Intern. Ed. Engl.*, **3**, 453 (1964).

(19) L. M. Venanzi, cited in ref 20, p 164.

(20) C. K. Jørgensen, "Inorganic Complexes," Academic Press Inc. London, 1963, p 162.

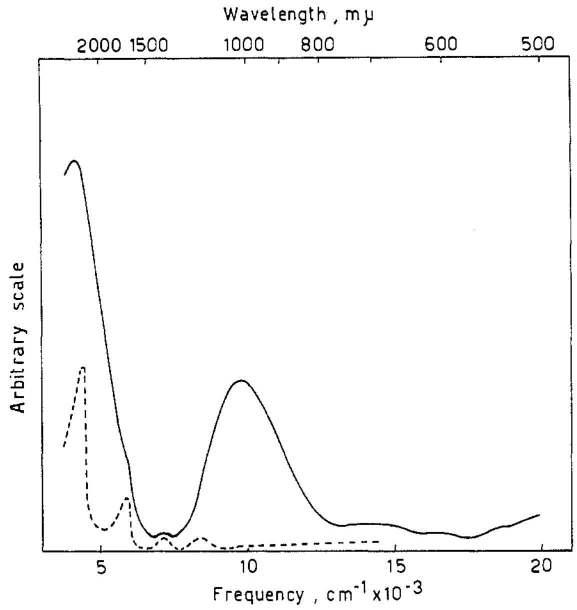

Figure 1.—Reflectance spectra of [Fe(Me$_6$tren)Br]Br (solid line) and [Zn(Me$_6$tren)Br]Br (dotted line).

between the three orbital levels, which originate from the splitting of the fundamental term $^5$D(3d$^6$) of Fe$^{2+}$ in a crystal field of the point group C$_{3v}$.

Plausible figures for the crystal-field parameters are $\beta = 80°^{15,16}$ and $\mu_5/\mu_1 = 0.9$.[21-23] If $\nu_2[^5E(2) \rightarrow {}^5A_1]$ is assigned to 9800 cm$^{-1}$—this requires $\mu_1 = 2.75$ D.—$\nu_1[^5E(2) \rightarrow {}^5E(1)]$ is reached at 3100 cm$^{-1}$.

This assignment is substantiated by analyses of the spectra of [Cr(Me$_6$tren)Br]Br which has very likely a closely similar geometry.[5] It is, in fact, well known that the splitting of the $^5$D state, which is also fundamental for the d$^4$ configuration, is the same as that for the d$^6$ configuration, except that the sign of the energies is reversed. Using the above-mentioned values of the $\beta$ and $\mu$ parameters, two spin-allowed transitions, $^5A \rightarrow {}^5E(1)$ at 10,000 cm$^{-1}$ and $^5A \rightarrow {}^5E(2)$ at 15,000 cm$^{-1}$, are anticipated. These frequencies are in satisfactory agreement with the maxima of the band (obtained by an analysis of the spectrum assuming Gaussian curves) which are 10,800 cm$^{-1}$ ($\epsilon$ 86, $P = 12.0 \times 10^{-4}$) and 14,000 cm$^{-1}$ ($\epsilon$ 32, $P = 3.5 \times 10^{-4}$), respectively.[5] The lower intensity of the second band may be accounted for in this electrostatic model, by assuming mixing of 4p and 3d metal orbitals. In fact, the second transition is forbidden in D$_{3h}$ symmetry and is only allowed in C$_{3v}$ symmetry as a consequence of the deviation of the $\beta$ angle from the value of 90°.

The spectrum of the [Cu(Me$_6$tren)Br]Br complex with bands at 10,300 cm$^{-1}$ ($\epsilon$ 450, $P = 5.4 \times 10^{-3}$) and 13,500 cm$^{-1}$ ($\epsilon$ 180, $P = 1.4 \times 10^{-3}$) is similar to that of the chromous analog. A similar interpretation holds for the spectrum of this copper compound bearing in mind that the D terms of the d$^4$ and d$^9$ configurations split in a qualitatively analogous manner.

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## Appendix

The well-known weak-field technique has been used.[24] The crystalline field is simulated by an array of five-point dipoles—belonging to point group C$_{3v}$—which surrounds the metal ion. The strength $\mu$ of the dipoles must be regarded as a semiempirical parameter in order to allow for many of the approximations of this model.

It is worth calling $\Psi(M_L) = \Psi(L, S, M_L, M_S)$ where $L = 2$, $S = 2$, and $(m|V|m') = \int \chi^*(m)(\Sigma_L V_L)\chi(m')\, d\tau$ where $\chi(m) = 3d_m$ metal orbital and $V_L$ is the electrostatic potential set up by each ligand L. Then, the orbital wave functions and energies for the $^5$D term of d$^4$ configuration are as follows (with the d$^6$ configuration of Fe$^{2+}$ the sign of the integrals $(m|V|m')$ must be reversed)

$$^5A_1 = \Psi(0)$$

$$^5E(1) = \sin\delta\,\Psi(1) - \cos\delta\,\Psi(\bar{2})$$

$$= \sin\delta\,\Psi(\bar{1}) - \cos\delta\,\Psi(2)$$

$$^5E(2) = \cos\delta\,\Psi(1) + \sin\delta\,\Psi(\bar{2})$$

$$= \cos\delta\,\Psi(\bar{1}) + \sin\delta\,\Psi(2)$$

$$E[^5A_1] = 2[(2|V|2) + (1|V|1)]$$

$$E[^5E(1)] = 2(2|V|2) + (1|V|1) + (0|V|0) - (2|V|-1)\cot\delta$$

$$E[^5E(2)] = (2|V|2) + 2(1|V|1) + (0|V|0) + (2|V|-1)\cot\delta$$

where

$$\delta = {}^1/_2 \arctan\{2(2|V|-1)[(2|V|2) - (1|V|1)]^{-1}\}$$

In the present calculations the metal dipole distances have been thoroughly taken as 2.00 A. The analysis of the spectroscopic term separations for the free ions Cr$^{2+}$ and Fe$^{2+}$,[25] by means of Condon–Shortly parameters suggests values for the nuclear effective charge of about 6.00 and 7.15, respectively. As usual these figures have been then reduced by 15% in order to allow for nephelauxetic effects. The integrals $(m|V|m')$ have been calculated by using Ballhausen and

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(21) Ammonia and ethylenediamine produce stronger crystalline fields, as measured by the $Dq$ values of octahedral complexes, than bromide ion. Thus a ratio $Dq$(bromide)/$Dq$(amine) = 0.6, is usually found (ref 22). N-Methylated ethylenediamines, however, give lower $Dq$ values probably because of steric hindrance to coordination (ref 23). The $Dq$ sequence of octahedral nickel–ethylenediamine complexes with increasing methyl substitution suggest a ratio $\mu_5/\mu_1 \approx 0.9$ in the case of the present ligand.

(22) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., London, 1962, p 113.

(23) S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 20 (1965).

(24) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(25) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular 476, Vol. 2, U. S. Government Printing Office, Washington, D. C., 1952.

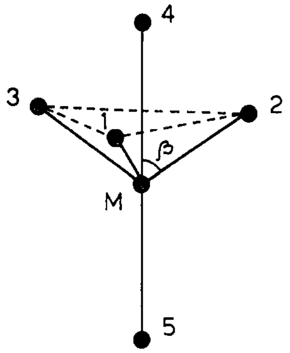

Figure 2.—A sketch of the coordinates used in thec rystal-field calculation.

Ancmon tables.[26] In every case it has been put $\mu_1 = \mu_2 = \mu_3 = \mu_4$ (see Figure 2 for numbering of the dipoles). The energy of the $Cr^{2+}$ and $Fe^{2+}$ levels, split in fields of $C_{3v}$ symmetry, are reported in Table IV for several values of the parameters $\beta$ and $\mu_5$.

TABLE IV

ENERGY LEVELS OF THE TERMS $^5D$ ($3d^4$ AND $3d^6$) IN CRYSTALLINE FIELDS OF $C_{3v}$ SYMMETRY[a]

| $\beta$, deg | $\mu_5/\mu_1$ | | $E[^5A_1]/\mu_1$, $cm^{-1}$ D.$^{-1}$ | $E[^5E(1)]/\mu_1$, $cm^{-1}$ D.$^{-1}$ | $E[^5E(2)]/\mu_1$, $cm^{-1}$ D.$^{-1}$ |
|---|---|---|---|---|---|
| 90 | 1.0 | Cr | −3960 | +200 | +1780 |
| | | Fe | +2620 | −230 | −1080 |
| | 0.8 | Cr | −3460 | −60 | +1790 |
| | | Fe | +2260 | −20 | −1110 |
| 85 | 1.0 | Cr | −3920 | +170 | +1790 |
| | | Fe | +2620 | −210 | −1100 |
| | 0.8 | Cr | −3420 | −80 | +1790 |
| | | Fe | +2260 | −20 | −1110 |
| 80 | 1.0 | Cr | −3840 | +60 | +1860 |
| | | Fe | +2590 | −120 | −1170 |
| | 0.8 | Cr | −3340 | −150 | +1820 |
| | | Fe | +2220 | +30 | −1140 |

[a] The baricenter of these levels has been taken as the zero of the energy.

[26] C. J. Ballhausen and E. M. Ancmon, *Kgl. Danske Videnskab. Selskab, Mat Fys. Medd.*, **29**, 4 (1954).

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CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY,
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# Coordination in Solutions. IV. Association Constants for 1:1 Complexes of Cu(II), Zn(II), Ca(II), La(III), and Y(III) with Anions of Salicylaldehydes[1,2]

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Association constants for 1:1 complexes of Cu(II), Zn(II), Ca(II), La(III), and Y(III) are reported at 25° and an ionic strength of 0.1 *M* in aqueous solution. The ligands were the anions of the parent and of the 3-, 4-, 5-, 6-chloro, 3-, 5-nitro, and 3,5-dinitro derivatives of salicylaldehyde. Constants are reported for the association of La(III) with the anions of phenol, *o*-nitrophenol, and *o,p*-dinitrophenol and for Y(III) with phenol anion. $\pi$ bonding, if it occurs in the Cu(II) complexes, has no detectable effect on trends in stability. Generalized and special case treatments are presented to obtain complex constants from spectrophotometric data where three absorbing species change concentration.

Irregularities in the relative stability of 1:1 Cu(II) complexes with anions of salicylaldehyde and derivatives in aqueous–dioxane solutions have been attributed to variations in $\pi$ bonding involving d electrons from the Cu(II).[3–5] This proposal is examined in the present work by comparison of the Cu(II) complex stabilities in aqueous solution with those of noble gas structure cations. Two of the monochloro derivatives of salicylaldehyde have been reassigned as 4- and 6-chloro isomers,[6] invalidating some of the previous observations.[3,4] Generalized and special case treatments of spectrophotometric data for systems of three absorbing species are presented. The acid dissociation constants have been reported previously.[6,7]

## Experimental Section

**Materials.**—The preparation and purification of the chelating acids and the inorganic reagents have been reported previously.[2,6–8] Perchlorate stock solutions of $Cu^{2+}$, $Zn^{2+}$, $Y^{3+}$, and $La^{3+}$ were prepared by reaction of the oxides with excess perchloric acid. Perchlorate stock solutions of $Ca^{2+}$ were prepared by the reaction of perchloric acid with three calcium salts: (1) reagent grade carbonate, (2) carbonate prepared from reagent grade chloride (the latter contained a smaller concentration of interfering metals than reagent grade carbonate), and (3) reagent grade chloride. In method 3, a chloride-free solution was obtained by repeated evaporation of excess perchloric acid. The $Cu^{2+}$ stock was analyzed by electrodeposition. The other metal stocks were analyzed in two ways: gravimetrically as sulfate by evaporation and ignition at 400° of an aliquot to which an excess of sulfuric acid had been added, and by titration of the hydrogen ion liberated from a cation-exchange column (Dowex

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Part III: L. B. Magnusson, C. A. Craig, and C. Postmus, Jr., *J. Am. Chem. Soc.*, **86**, 3958 (1964).

[3] J. G. Jones, J. B. Poole, J. G. Tomkinson, and R. J. P. Williams, *J. Chem. Soc.*, 2001 (1958).

[4] K. Clarke, R. A. Cowen, G. W. Gray, and E. H. Osborne, *ibid.*, 245 (1963).

[5] B. R. James, M. Parris, and R. J. P. Williams, *ibid.*, 4630 (1961).

[6] Part II: C. Postmus, Jr., I. A. Kaye, C. A. Craig, and R. S. Matthews, *J. Org. Chem.*, **29**, 2693 (1964).

[7] Part I: L. B. Magnusson, C. Postmus, Jr., and C. A. Craig, *J. Am. Chem. Soc.*, **85**, 1711 (1963).

[8] I. A. Kaye, R. S. Matthews, and A. A. Scala, *J. Chem. Soc.*, 2816 (1964).