TABLE II

MOLAR ABSORPTIVITIES ($\times 10^{-3}$) OF TRIS(2-PYRIDINALIMINE)- AND TRIS(2-PYRIDYL KETOIMINE)IRON(II) COMPLEXES IN DEPENDENCE UPON R AND R′ IN I. SOLVENT, 20% BY VOLUME OF METHANOL IN WATER; 23 ± 2°

	R′		
R	H	CH_3	C_6H_5
H	...	11	8
CH_3	13	11.5	9.5
C_6H_5	17	14	12.5

discussed by Favini and Simonetta.[13] For the corresponding aza analogs[14] presently considered, twisting angles are likely to follow the same order, *viz.*, H,$\mathit{C_6H_5}$ < $\mathit{C_6H_5}$,H < $\mathrm{C_6H_5}$,$\mathit{C_6H_5}$ < $\mathit{C_6H_5}$,$\mathrm{C_6H_5}$ < $\mathrm{CH_3}$,$\mathit{C_6H_5}$ < $\mathit{C_6H_5}$,$\mathrm{CH_3}$ where substituents are listed in the order R,R′ and $\mathit{C_6H_5}$ is the phenyl group whose twisting angle is considered. Inspection of Table I shows that the bathochromic effect of replacing methyl by phenyl decreases exactly in the order of increasing twisting angles of the phenyl groups concerned (the corresponding order of the spectral shifts is 23-18-14-11-10-7 mμ). This correlation between twisting angles and the spectral effect of phenyl substituents also provides an easy explanation for the hypsochromic effect of replacing hydrogen by methyl in the H,C_6H_5 complex, as compared with the opposite effect of the same substitution in the H,CH_3 derivative (see Table I).

The spectral effect of amino substituents in the 2-pyridyl N-arylketimine complexes depends on the position of the free amino group. Absorption maxima of the iron(II) complexes of the 3-aminophenylketimines and of the unsubstituted phenylketimines are practically the same. 4-Amino substituents produce a bathochromic shift of about 10 mμ. The 2-aminophenyl derivatives behave as tridentate ligands[15] and are thus not directly comparable with the other isomers.

The molar absorptivities of the complexes at their respective absorption maxima, listed in Table I, are summarized in Table II. Absorptivities increase on passing from the 2-pyridinalimine complexes to the complexes of the methyl 2-pyridyl and particularly the phenyl 2-pyridyl ketoimines. Curiously, changing the substituents on the imino nitrogen affects intensities in just the opposite direction.

The absorption spectra of the two forms of the 2-pyridyl N-arylketimine complexes are substantially alike, except for the position of the absorption maxima. When R is methyl, the absorption maximum of the labile form is shifted by approximately 3 mμ toward longer wave lengths, as compared with the maximum of the stable form. When R is phenyl, the difference amounts to approximately 10 mμ.

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[13] G. Favini and M. Simonetta, *Theoret. Chim. Acta*, **1**, 294 (1963).

[14] 2-Pyridinalphenylimine is compared to *trans*-stilbene, phenyl 2-pyridyl ketimine to 1,1 diphenylethylene, etc.

[15] P. Krumholz, *Inorg. Chem.*, **4**, 612 (1965).

CONTRIBUTION FROM THE RESEARCH LABORATORY
OF ORQUIMA S.A., SÃO PAULO, BRAZIL

Studies on the Coordinate Bond. VI. The Nature of the Chromophoric Group in Iron(II) Complexes of Tridentate Imine Ligands[1]

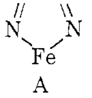
BY P. KRUMHOLZ

Received June 15, 1964

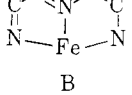
The visible absorption spectra of iron(II) complexes of a series of "terpyridine-like" tridentate imine ligands containing the functional grouping $N{=}C{-}C{=}N{-}C\cdot C\cdot N$ have been recorded. Independently of the nature of bonding in the $C\cdot C\cdot N$ chain, these complexes belong to a single chromophoric class. The specific spectral pattern which characterizes this class is correlated with the fusing of a second chelate loop on the iron(II)–α-diimine ring. The resulting spatial structure and mutual orientation of metal and ligand orbitals may cause a significant distortion of the ligand field from cubic symmetry. Splitting of the metal t_{2g} orbitals by noncubic field components is held responsible for the appearance of a new transition in the spectra of the tridentate imine complexes.

Introduction

It is well established[2,3] that the octahedral iron(II) complexes of bidentate α-diimine ligands such as 2,2′-bipyridine, 2-pyridinalmethylimine, and glyoxalbismethylimine constitute a single class of compounds with very similar spectral properties. The cyclic iron(II)–α-diimine grouping A can be considered as the common structural element or "chromophore."[4]



A



B

In the iron(II) complexes of the related tridentate imine ligands such as terpyridine,[5] a second chelate ring is fused on the iron(II)–α-diimine ring, as pictured in B. It is the object of this study to investigate the

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[1] Part V: P. Krumholz, *Inorg. Chem.*, **4**, 609 (1965).

[2] P. Krumholz, *J. Am. Chem. Soc.*, **75**, 2163 (1953).

[3] D. H. Busch and J. C. Bailar, Jr., *ibid.*, **78**, 1137 (1956).

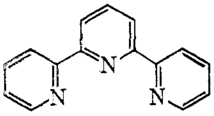
[4] It is tacitly assumed that three of these "chromophores" are actually present and linked through the common central metal.

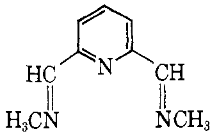
[5] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 20 (1932).

effect of such ring fusion or annelation on the spectral properties of the respective iron(II) complexes.

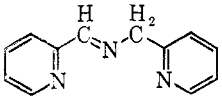
A considerable number of "terpyridine-like" tridentate ligands and their iron(II) complexes have recently become available, chiefly through the work of Lions and co-workers.[6–8] Absorption spectra, however, have only been reported for the complexes of terpyridine itself[9] and some of its substitution products.[10]

In order to obtain information on the chromophoric properties of the fused chelate ring system B, the visible absorption spectra of the iron(II) complexes of suitably chosen or designed tridentate imine ligands have been determined. The complex ions, [Fe(ligand)$_2$]$^{2+}$, of the following ligands have been investigated: I, 2,6-bis(2′-pyridyl)pyridine (terpyridine)[5]; II, 2,6-pyridinedialbismethylimine[11]; III, 2-(2′-pyridylmethyleneaminomethyl)pyridine[6,12]; IV, 1-(2′-pyridylmethyleneamino)-2-aminoethane[13] V, 1-[1′-(2′-pyridyl)-ethylideneamino]-2-aminoethane; VI, 1-(2′-pyridylmethyleneamino)-2-aminobenzene; and VII, 8-(2′-pyridylmethyleneamino)quinoline.[14]

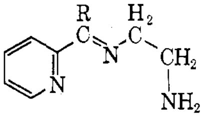

I



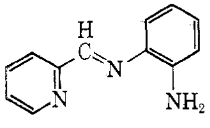
II



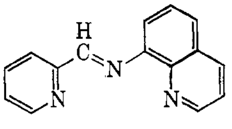
III



IV, R=H
V, R=CH$_3$



VI



VII

Experimental

Preparation of Compounds.—The iron(II) complexes of ligands I, II, III, and VII were prepared according to the procedures described in the literature and isolated as iodides or perchlorates.

Bis[1-(2′-pyridylmethyleneamino)-2-aminoethane]iron(II) Iodide.—To a solution of 1.32 g. (22 mmoles) of ethylenediamine in 12 ml. of water at 40° was added dropwise a solution of 2.14 g. (20 mmoles) of pyridine-2-aldehyde in 10 ml. of ethanol. The mixture was kept at 40° for 10 min. and 15 ml. of a 0.66 *M* aqueous solution of ferrous chloride (10 mmoles) was added while passing nitrogen through the reaction mixture. After 10 min. standing at room temperature, 5 g. of potassium iodide was added and the mixture kept at −5° for 2 hr. The dark violet, microcrystalline precipitate was filtered off, washed with a solution of potassium iodide, and finally with a few ml. of water; yield, 5 g.

Anal. Calcd. for [Fe(C$_8$H$_{11}$N$_3$)$_2$]I$_2$: Fe, 9.18; N, 13.82; I, 41.75. Found (dried *in vacuo* over P$_2$O$_5$): Fe, 9.15; N, 13.6; I, 41.5.

Bis[1-(2′-pyridylmethyleneamino)-2-aminoethane]iron(II) Perchlorate.—This compound was prepared similarly to the corresponding iodide using sodium perchlorate as precipitating agent instead of potassium iodide; yield, 5 g. of dark violet crystals.

Anal. Calcd. for [Fe(C$_8$H$_{11}$N$_3$)$_2$](ClO$_4$)$_2$: Fe, 10.10; N, 15.20. Found (dried *in vacuo* over P$_2$O$_5$): Fe, 10.05; N, 15.3.

Bis[1-{1′-(2′-pyridyl)ethylideneamino}-2-aminoethane]iron(II) Perchlorate.—To a mixture of 0.7 g. of a 60% aqueous solution of ethylenediamine (7 mmoles) and 4 ml. of ethanol at 40° was added a solution of 0.6 g. (5 mmoles) of methyl 2-pyridyl ketone (F. Raschig, G.m.b.H., Ludwigshafen) in 1 ml. of ethanol. The mixture was heated at 40° under nitrogen for 2 hr., 6.25 ml. of 0.4 *M* aqueous ferrous chloride (2.5 mmoles) was added, and heating was continued under nitrogen for 2 hr. The solution was filtered, 2 g. of sodium perchlorate was added, and the mixture was kept at 0° for 2 hr. The dark violet, microcrystalline precipitate was filtered off and washed with a solution of sodium perchlorate and finally with a few ml. of water; yield, 1.4 g.

Anal. Calcd. for [Fe(C$_9$H$_{13}$N$_3$)$_2$](ClO$_4$)$_2$: Fe, 9.61; N, 14.46. Found (dried *in vacuo* over P$_2$O$_5$): Fe, 9.65; N, 14.5.

Bis[1-(2′-pyridylmethyleneamino)-2-aminobenzene]iron(II) Iodide.—To a solution of 2.4 g. (22 mmoles) of *o*-phenylenediamine in 15 ml. of ethanol at 40° was added dropwise in an atmosphere of nitrogen 2.14 g. (20 mmoles) of pyridine-2-aldehyde. The mixture was kept at room temperature for 10 min. and 15 ml. of 0.66 *M* ferrous chloride (10 mmoles) was added. Potassium iodide (5 g.) precipitated from the deep blue solution a product which contained an appreciable amount of chloride. It was dissolved in 700 ml. of water at 50°, the solution was filtered, 5 g. of potassium iodide was added, and the mixture was kept at room temperature for 2 hr. The blue, microcrystalline precipitate was filtered off and washed with a 1% solution of potassium iodide until the color of the wash water became pure blue and finally with a 1:1 ethanol–ether mixture until the filtrate became colorless; yield, 3.5 g.

Anal. Calcd. for [Fe(C$_{12}$H$_{11}$N$_3$)$_2$]I$_2$: Fe, 7.93; N, 11.94; I, 36.05. Found (dried *in vacuo* over P$_2$O$_5$): Fe, 7.9; N, 11.7; I, 35.0; Cl, 0.15.

Spectrophotometric Measurements.—The absorption spectra of the iron(II) complexes of ligands I to VII in aqueous solution at 23 ± 2° were determined in the range between 400 and 750 mμ. A grating instrument previously described[15] was used at a band width of 0.2 mμ. Reported absorption maxima are believed to be correct to within ±2 mμ.

Results

The visible absorption spectra of the iron(II) complexes of representative tridentate imine ligands are shown in Figures 1 and 2. Absorption maxima are given in Table I, together with the relevant structural details of the ligands.

Despite significant structural differences between individual ligands, the iron(II) complexes of all tridentate imine ligands seem to belong to a single spectral class. With the apparent exception of the terpyridine (I) complex, the shapes of all band envelopes in Figures 1 and 2 are alike. On the other hand, the shapes differ substantially from the form of the visible absorption band of the iron(II) complexes of bidentate α-diimine

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[6] F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **79**, 2733 (1957).

[7] H. A. Goodwin and F. Lions, *ibid.*, **81**, 6415 (1959).

[8] J. F. Geldard and F. Lions, *Inorg. Chem.*, **2**, 270 (1963).

[9] M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **14**, 862 (1942).

[10] G. F. Smith and W. M. Banick, *Anal. Chim. Acta*, **18**, 269 (1958).

[11] P. F. Figgins and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 820 (1960).

[12] P. Krumholz, *Inorg. Chem.*, **4**, 757 (1965).

[13] H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **82**, 5013 (1960), prepared the iron(II) complex of the corresponding 6′-methyl-2′-pyridyl derivative.

[14] F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *ibid.*, **75**, 3834 (1953).

[15] P. Krumholz, *Spectrochim. Acta*, **10**, 274 (1958).

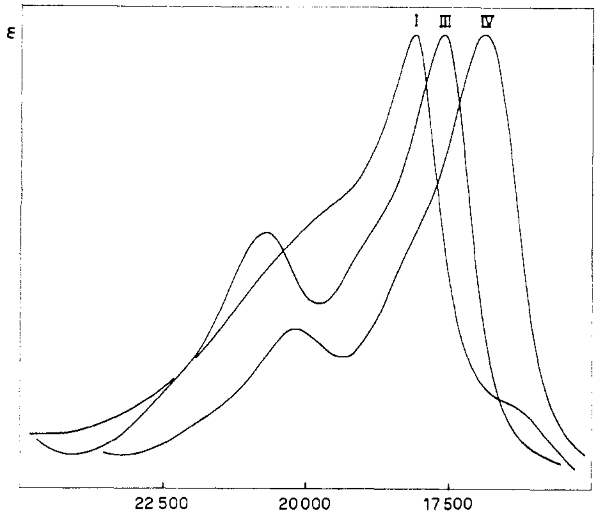


Figure 1.—Absorption spectra of aqueous solutions of iron(II) complexes of tridentate imine ligands. Numbers refer to ligands listed in the Introduction. Curves are drawn to equal height at the main absorption maximum. The numerical values of the molar absorbancy indices at these maxima are: I, 1.15×10^4; III, 1.1×10^4; IV, 1.2×10^4.

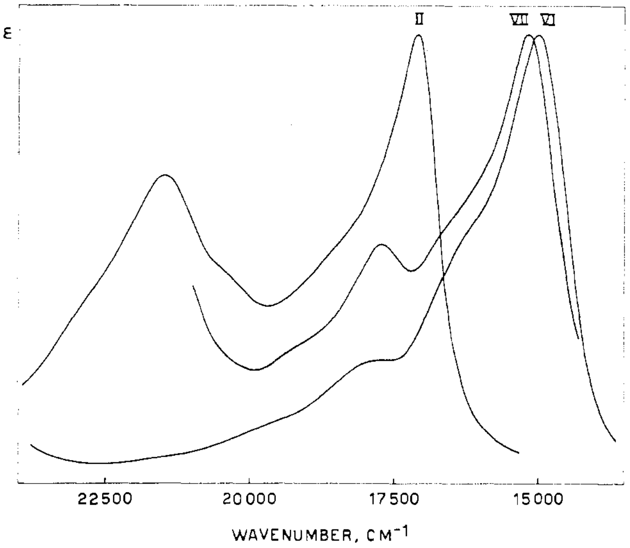


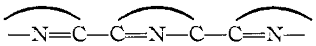
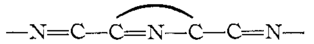
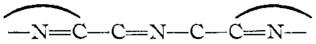
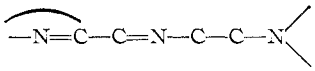
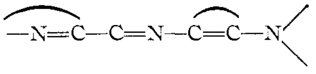
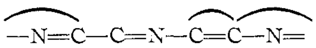
Figure 2.—Absorption spectra of aqueous solutions of iron(II) complexes of tridentate imine ligands. Numbers refer to ligands listed in the Introduction. Curves are drawn to equal height at the main absorption maximum. The numerical values of the molar absorbancy indices at these maxima are: II, 1.15×10^4; VI, 7.5×10^3; VII, 6.5×10^3.

ligands, which remains nearly invariant in a large number of derivatives.[2,16]

The main absorption band of the iron(II) complexes of the tridentate imine ligands is remarkably narrow, the half-width toward smaller wave numbers, $\delta(-)$,[17] varying between about 450 and 650 cm.$^{-1}$. This may be compared with $\delta(-)$ of 900 ± 100 cm.$^{-1}$ for the visible band of the bidentate α-diimine complexes.[18]

TABLE I

STRUCTURE OF TRIDENTATE IMINE LIGANDS AND ABSORPTION MAXIMA, λ_{max} (IN mμ), OF THEIR IRON(II) COMPLEXES

Ligand	Structure[a]	λ_{max}	
I	 —N=C—C=N—C—C=N—	552	. . .
II	 —N=C—C=N—C—C=N—	585	466
III	 —N=C—C=N—C—C=N—	568	483
IV	 —N=C—C=N—C—C—N<	592	496
V		597	503
VI	 —N=C—C=N—C=C—N<	667	560
VII	 —N=C—C=N—C=C—N=	659	564

[a] Arcs denote atoms which belong to aromatic rings.

Toward larger wave numbers, a shoulder appears at a distance of 1200–1500 cm.$^{-1}$ from the main band maximum. This shoulder is less pronounced than the one observed for the spectra of the iron(II) complexes of bidentate α-diimine ligands and which has been tentatively assigned to a transition to a vibrationally-excited upper state.[16] At still larger wave numbers, a distinct second peak appears in the spectra of the iron(II) complexes of all tridentate imine ligands except terpyridine. In the latter complex, this transition is likely to be masked by the very broad shoulder which extends to about 3000 cm.$^{-1}$ from the single absorption maximum. In the spectra of the iron(II) complexes of ligands III, IV, V, VI, and VII, the second peak is situated at a distance of 2550–3300 cm.$^{-1}$ from the main band maximum. This peak is also accompanied by a weak shoulder toward larger wave numbers. In the spectrum of the 2,6-pyridinedialbismethylimine (II) complex, the distance between the two peaks is increased to about 4400 cm.$^{-1}$. Furthermore, the second peak displays an additional shoulder toward smaller wave numbers at a distance of about 1200 cm.$^{-1}$. Unless this shoulder represents a higher vibrational component of the main absorption band, the presence of one further electronic transition must be acknowledged. Finally, the shoulder observed on the long wave length wing of the single absorption band of the iron(II) terpyridine complex must likely be assigned to a separate electronic transition.

The nature of bonding in the N·C·C·N·C·C·N ligand skeleton which forms the fused chelate ring system B visibly affects the position of the absorption maxima of the respective iron(II) complexes. Considering first the structurally similar ligands I, II, and III, one observes that the main absorption band of the corresponding iron(II) complexes shifts toward the blue as the number of aromatic rings in the ligand increases. Busch and Bailar[3] have already noted the same trend in the series of iron(II) complexes of bidentate α-diimine ligands. Ligands I, II, and III may formally be considered as "triimines" containing two conjugated and one isolated C=N double bonds. When the latter is replaced by a single bond (*viz.* ligands IV and V), the absorption maxima of the

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[16] P. Krumholz, "Theory and Structure of Complex Compounds," B. Jeżowska-Trzebiatowska, Ed., Pergamon Press, Warszawa, 1964, p. 217.

[17] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p. 93.

[18] P. Krumholz, unpublished results.

iron(II) complexes are found to move, rather unexpectedly, toward the red. On the other hand, when this double bond is shifted to a position where it may enter into the conjugation already present (*viz.* ligands VI and VII), the absorption maxima move still further toward the red. Lengthening of the system of conjugated double bonds within the atomic skeleton which forms the chelate ring system B thus produces a strong bathochromic effect. Comparing ligands VI and VII, one finds again that increasing the number of aromatic rings in the ligand causes a blue shift of the main absorption band of the respective iron(II) complex.

Molar absorptivities at the main absorption maxima of the iron(II) complexes of ligands I to V are nearly identical (ϵ_{max}, 1.1×10^4–1.2×10^4). Considerably lower values are found for the complexes of ligands VI and VII (ϵ_{max}, 7.5×10^3 and 6.5×10^3, respectively).

Discussion

The spectral behavior of the iron(II) complexes of the tridentate imine ligands listed in the Introduction suggests once more[2,3] the presence of a single structural element or "chromophore" throughout the series. Inspection of the structural data in Table I reveals that this chromophore is associated with a N=C—C=N—C·C·N grouping (points denote single or double bonds) linked, as pictured in B, through all three nitrogens to the central metal. The fused chelate ring system B will thus be considered as the proper chromophore, making, however, due allowance for the fact that actually two of these chromophores are present and linked through the common central metal.

The spectral pattern of the iron(II) complexes of the tridentate imine ligands depends only little on the nature of the bonding in the second chelate loop of B fused on the iron(II)–α-diimine ring. In particular, it is of minor importance whether this loop does or does not contain a double bond and whether this double bond is conjugated with the α-diimine grouping. The mere fact of closing the second chelate loop in B therefore seems responsible for the change of the spectral pattern as one passes from the complexes of the bidentate α-diimines to those of the tridentate imine ligands.[19] It follows that at least some of the factors governing the spectral pattern are connected with the molecular architecture of the complex ions. Discussion of such factors presupposes a basic understanding of the nature of the electronic transitions which are responsible for the visible absorption spectra of the complexes here considered.

According to Williams[20] and Jørgensen,[21] the visible absorption of iron(II)–tris-α-diimine complexes is caused by an electron transfer from the metal to the ligands. Despite the lower over-all symmetry (D_3 or lower), the local symmetry of the field around the central metal may be considered, to a good approximation, as cubic (O_h). In this case and since the above complexes are spin-paired, the orbitals to be considered are the filled t_{2g} orbitals of the metal (or mainly localized on the metal) and the empty π^*-orbitals of the ligands (or mainly localized on the ligands).

Geometrical considerations lead one to expect that in the case of the iron(II) complexes of tridentate imine ligands, $[Fe(ligand)_2]^{2+}$, noncubic field components will become rather important. Molecular models and available structural data (*e.g.*, for Zn(terpy)-Cl_2[22]) show that the central metal and the terminal nitrogens of the ligands are unlikely to lie all in a single plane. The local symmetry determined by the placement of the nitrogens about the central metal will then become D_{2d} (which is the maximum over-all symmetry of the complex, even if all N–Fe–N angles are 90°). On the other hand, as pointed out by Figgins and Busch,[23] π-bonding involving the filled metal d-orbitals and the empty ligand π^*-orbitals (back donation) should lead to a tetragonal (D_{4h}) distortion, because the mutual orientation of the orbitals favors back donation toward the central nitrogens of the ligands. The large quadrupole splitting observed recently[24,25] in the Mössbauer spectra of iron(II) complexes of terpyridine and other tridentate imine ligands seems to confirm the predicted distortion from cubic symmetry.

The lowering of the symmetry from O_h to D_{4h} or D_{2d} will cause a splitting of the threefold degenerate t_{2g} level into one single and one twofold degenerate level ($b_{2g} + e_g$ in D_{4h} or $b_2 + e$ in D_{2d}). It is believed that such splitting is responsible for the apearance of the second peak in the visible spectra of the iron(II) complexes of tridentate imine ligands.

It has been noted before that the main absorption band of the complexes of tridentate imine ligands is much narrower than that of the bidentate α-diimine complexes. This might be connected with the greater rigidity (or lesser deformability) of the fused chelate ring system B, which will tend to restrain the molecule from changing its equilibrium configuration when excited.[26] Now, the very likely coplanar chelate ring systems formed by ligands I and II should be stiffer than those formed by ligands IV and V and which contain an aliphatic and probably nonplanar chelate loop. In fact, one finds that the bands of the complexes of the latter ligands are broader ($\delta(-)$ about 650 cm.$^{-1}$) than these of the complexes of ligands I and II ($\delta(-)$ 440 and 530 cm.$^{-1}$, respectively).

The effect of fusing an aliphatic chelate loop on the iron(II)–α-diimine ring will mainly consist in imposing certain steric conditions on the complex. The π^*-orbitals which take part in the electron-transfer process will still be confined to the iron(II)–α-diimine ring.

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(19) This conclusion is corroborated by the spectral behavior of iron(II) complexes of ligands such as 1-(2′-pyridylmethyleneamino)-2-diethylaminoethane which, while containing the potentially tridentate N=C—C=N—C·C·N grouping, actually behaves as a bidentate ligand. The spectrum of the iron(II) complex of this ligand[16] is quite different from the spectra of the complexes of ligands I to VII and belongs unmistakably to the class associated with the iron(II)–α-diimine chromophore A.

(20) R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

(21) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 166 (1957).

(22) D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1956).

(23) P. E. Figgins and D. H. Busch, *J. Phys. Chem.*, **65**, 2236 (1961).

(24) L. M. Epstein, *J. Chem. Phys.*, **40**, 435 (1964).

(25) J. Danon, private communication.

(26) See L. E. Orgel, *J. Chem. Phys.*, **23**, 1824 (1955).

Presence of an isolated double bond in the second chelate loop of chromophore B is apparently of minor importance. However, if this double bond is conjugated with the α-diimine grouping (direct) electronic effects become operative. The large bathochromic effect of such "intrachromophoric" conjugation strongly suggests that the π*-orbitals involved now become delocalized in the second chelate loop.

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Cobalt(III) Complexes of *trans*-1,2-Cyclopentanediamine[1]

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The cobalt(III) complexes of *trans*-1,2-cyclopentanediamine have been reinvestigated. The preparative methods used by the previous workers were found to be unsatisfactory, and more satisfactory procedures were developed. The ion previously reported to be $[Co(cptdin)_3]^{3+}$ was found to be $[Co_2(cptdin)_7(H_2O)_2]^{6+}$ and a structure which contains no chelate rings is proposed for this ion. This structure is consistent with the experimental data, and it explains the completely stereospecific character of this ion. During the course of the work a procedure was developed for the chemical determination of noncoordinated primary amine groups in an inert complex. A specialized procedure for the determination of the charge on a highly charged cation was also developed.

Introduction

Many years ago Jaeger and Blumendal[2] made one of the most significant of the early investigations of the stereochemical behavior of complex ions containing asymmetric ligands in which they studied the cobalt(III) and rhodium(III) complexes of *trans*-1,2-cyclopentanediamine (cptdin). They prepared compounds which were reported to contain the ions $[M(cptdin)_3]^{3+}$, $[M(cptdin)_2Cl_2]^+$, $[M(en)_2(cptdin)]^{3+}$, and $[M(en)(cptdin)_2]^{3+}$, where M is Co or Rh, and determined the optical configuration of the metal ion environment and of the ligands. Of the numerous possible isomers which could be postulated for these ions they were able to obtain evidence for the existence of only the following enantiomorphic pairs: D,L-$[M(l,d\text{-cptdin})_3]^{3+}$, D,L-*cis*-$[M(l,d\text{-cptdin})_2Cl_2]^+$, D,L-$[M(en)(l,d\text{-cptdin})_2]^{3+}$, and D- or L-$[M(en)_2(d\text{- or }l\text{-cptdin})]^{3+}$. On the basis of these findings and earlier investigations with other optically active bidentate ligands,[3-5] Jaeger attributed this drastic reduction in the number of isomers to the essentially exclusive formation of one preferred configuration, the complex tending to exist as the most symmetrical possible diastereoisomer.

Corey and Bailar[6] have considered the possible conformations of a tris-bidentate complex containing nonrigid five-membered ethylenediamine-type chelate rings. Their results indicate that while there is indeed a preferred diastereoisomer in these cases, it should be only approximately 2 kcal./mole more stable than the remaining diastereoisomers.

Experimental support of the views of Corey and Bailar has been provided by Dwyer and co-workers,[7] who have prepared a number of additional isomers in which the optically active ligand is propylenediamine.

Implicit in all of the conclusions drawn from Jaeger's work, both by Jaeger and by later workers,[6] is the assumption that the cptdin molecule functions as a reasonably normal bidentate ligand. However, a consideration of the geometry of the cyclopentane ring and the steric requirements for chelate ring formation shows that this assumption may be incorrect. Assuming that the cyclopentane ring has the same conformation in the cptdin molecule as it has in cyclopentane itself,[8] the minimum nitrogen–nitrogen distance in an unstrained conformation of the free diamine molecule is 3.5 Å., and the angle formed by the projection of the two carbon–nitrogen bonds when viewed down the intervening carbon–carbon bond is 109°. The corresponding values in the Co(en) chelate ring are 2.75 Å. and 48.8°. Thus severe bond angle strain is introduced by the *trans* fusion of two five-membered rings which would be necessary if cptdin is to act as a bidentate ligand.

In view of the above considerations, a reinvestigation of the Co(III)–cptdin complexes was undertaken.

Experimental

Preparation of cptdin.—The cptdin was prepared by the

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[2] F. M. Jaeger and H. B. Blumendal, *Z. anorg. allgem. chem.*, **175**, 161 (1928).

[3] P. Pfeiffer and T. H. Gassmann, *Ann.*, **346**, 59 (1906).

[4] L. Tschugaeff and W. Sokoloff, *Ber.*, **42**, 55 (1909).

[5] A. Smirnoff, *Helv. Chim. Acta*, **3**, 59 (1920).

[6] E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[7] (a) F. P. Dwyer, F. L. Garvan, and A. Shulman, *ibid.*, **81**, 290 (1959); (b) F. P. Dwyer and F. L. Garvan, *ibid.*, **81**, 1043 (1959); (c) F. P. Dwyer and A. M. Sargeson, *ibid.*, **81**, 5269 (1959); (d) F. P. Dwyer and A. M. Sargeson, *ibid.*, **81**, 5272 (1959); (e) F. P. Dwyer, A. M. Sargeson, and L. B. James, *ibid.*, **86**, 590 (1964).

[8] K. S. Pitzer, J. E. Kilpatrick, and R. Spitzer, *ibid.*, **69**, 2481 (1947).