As a matter of fact, none involve an attempt to observe the transformation and reaction independently. If the more general sense of the term is adopted, there is little question that such an effect occurs, although it most probably encompasses a whole class of phenomena, none of which are understood (see, for example, ref. 14).

(14) A. R. Ubbelohde, *Discussions Faraday Soc.*, **23**, 132 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASSACHUSETTS]

Studies on Ni(II) Complexes. I. Spectra of Tricyclic Schiff Base Complexes of Ni(II) and Cu(II)

BY RICHARD H. HOLM

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The relation between magnetism and stereochemistry is briefly summarized for complexes of quadricoördinate Ni(II) Complexes of the type $Ni-O_2N_2$ are seen especially likely to be distributed between planar spin-paired and spin-free forms. The spectra of a number of Ni(II) and Cu(II) complexes of the *cis* $M-O_2N_2$ type are reported. Ligand field strengths produced by salicylaldehyde- and acetylacetone-diimine ligand systems are compared, and it is shown that. as with the corresponding Cu(II) complexes, increase in the length of the methylene bridge is far more effective in weakening the ligand field than are ring substituents. The spectra of the Ni(II) complexes are discussed in relation to the singlet–triplet ground state separation and the ease of attaining partial paramagnetism in solution.

Introduction

The structures of complexes of quadricoördinate Ni(II) have been the subject of considerable discussion in recent years. Controversy has attended the assignment of tetrahedral stereochemistry to strictly four-coördinate complexes on the basis of their paramagnetism. This stereochemistry has been assigned in the past by many workers using the Pauling criterion for bond type,[1] which in the case of quadricoördinate Ni(II) states that paramagnetic complexes are $4s4p^3$ hybridized and tetrahedral whereas diamagnetic complexes are $4s3d4p^2$ bonded and planar. X-Ray structural determinations have been made on a number of diamagnetic four-coördinate complexes, such as potassium bis-(dithiooxalato) Ni(II),[2] Ni(II) phthalocyanine,[3] bis-(dimethylglyoxime) Ni(II),[4] bis-(salicylaldoxime) Ni(II),[5] dibromobis-(triethylphosphine) Ni(II),[6] bis-(salicylaldimine) Ni(II),[7] bis-(N-methylsalicylaldimine) Ni(II)[8] and all these have been shown to be planar. The increasing amount of structural information, recently summarized by Porai-Koshits,[9] emphasizes that many paramagnetic complexes once thought to be tetrahedral, *e.g.*, $Ni(en)_2(NCS)_2$,[10] $Ni(tren)(NCS)_2$,[11] $Ni(py)_2(NCS)_2$,[12] bis(salicylaldehyde) $Ni(II)\cdot 2H_2O$,[13] are in reality effectively six-coördinate in the solid, thus accounting for their paramagnetism. Indeed, as is now well recognized, evidence for the existence of discrete tetrahedral Ni(II) complexes is scant. Only recently has definite evidence been brought forth in the form of spectral, magnetic and dipole moment data to verify the existence of this class of complexes. The complexes $Ni[(C_6H_5)_3P]_2X_2$ ($X = Cl^-, Br^-, I^-, NO_3^-$) examined by Venanzi,[14] and $[(C_6H_5)_3AsCH_3]_2NiX_4$ ($X = Cl^-, Br^-, I^-$) studied by Nyholm[15a] and $Ni[(C_6H_5)_3MO]_2X_2$ ($M = P$, $X = Cl^-, Br^-, I^-$; $M = As$, $X = Cl^-, Br^-$) recently prepared by Cotton and Goodgame[15b] are almost certainly tetrahedral or pseudo-tetrahedral (C_{2v}).

The question remains as to the structures of other paramagnetic apparently four-coördinate (anhydrous) Ni(II) complexes of 8-hydroxyquinoline, *o*-hydroxyacetophenone, formylcamphor, anthranilic acid, acetylacetone,[16] salicylaldehyde,[16] and many others, all of which have magnetic moments in the range 3.0–3.3 B.M. Spin-free quadricoördinate complexes such as these have been little investigated, and there is no convincing evidence of any sort that any of these complexes are tetrahedral either in solution or in the solid. The same may be said for complexes paramagnetic in solution yet diamagnetic as solids.[17,18] It has been pointed out on several occasions[19,20] that quad-

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(1) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1948, pp. 112 ff.

(2) E. G. Cox, W. Wardlaw and K. C. Webster, *J. Chem. Soc.*, 1475 (1935).

(3) J. M. Robertson and I. Woodward, *ibid.*, 219 (1937).

(4) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

(5) L. L. Merritt, Jr., C. Guare and A. E. Lessor, Jr., *ibid.*, **9**, 253 (1956).

(6) G. Giacometti, V. Scatturin and A. Turco, *Gazz. chim. ital.*, **88**, 434 (1958).

(7) J. M. Stewart and E. C. Lingafelter, *Acta Cryst.*, **12**, 842 (1959).

(8) E. Frasson, C. Panattoni and L. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959).

(9) M. A. Porai-Koshits, *Russ. J. Inorg. Chem.* (Eng. trans.), **4**, 332 (1959).

(10) E. C. Lingafelter, *Nature*, **182**, 1730 (1958).

(11) S. E. Rasmussen, *Acta Chem. Scand.*, **13**, 2009 (1959).

(12) M. A. Porai-Koshits and G. N. Tishchenko, *Kristallografiya*, **4**, 239 (1959).

(13) E. C. Lingafelter, J. D. Breazeale, J. M. Stewart, Abstr. 4th IUC Int. Conf., Montreal, 1957, p. 56.

(14) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).

(15) (a) N. S. Gill, P. Pauling and R. S. Nyholm, *Nature*, **182**, 168 (1958); N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959). (b) F. A. Cotton and D. M. L. Goodgame, THIS JOURNAL, in press.

(16) Bis-(acetylacetonato) Ni(II) and bis-(salicylaldehyde) Ni(II) are probably not strictly four-coördinate. Preliminary X-ray studies [*cf.* G. J. Bullen, *Nature*, **177**, 537 (1956) and F. K. C. Lyle, B. Morosin and E. C. Lingafelter, *Acta Cryst.*, **12**, 938 (1959)] have indicated that, especially with the acetylacetonate, trimeric structures may exist in the solid.

(17) H. S. French, M. Z. Magee and E. Sheffield, THIS JOURNAL, **64**, 1924 (1942); B. Willis and D. P. Mellor, *ibid.*, **69**, 1237 (1947); F. Basolo and W. R. Matoush, *ibid.*, **75**, 5663 (1953); H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 3431 (1955); S. Fujii and M. Sumitani, *Sci. Rpts. Tohoku Univ.*, (Ser. 1) **37**, 49 (1953).

(18) L. Sacconi, P. Paoletti and G. Del Re, THIS JOURNAL, **79**, 4092 (1957); L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *ibid.*, **82**, 3487 (1960).

(19) C. J. Ballhausen, *Kgl. Danske. Vid. Mat. phys. Medd.*, **29**, No. 9 (1955).

(20) C. J. Ballhausen and A. D. Liehr, THIS JOURNAL, **81**, 538 (1959).

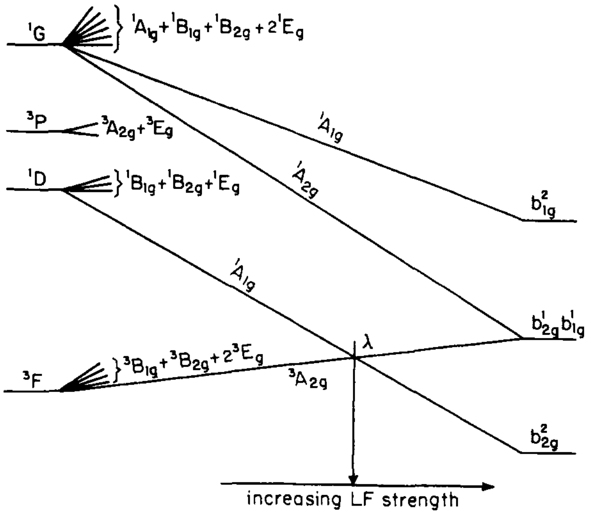

Fig. 1.—Simplified ligand field energy diagram for tetragonal Ni(II).

ricoördinate planar paramagnetic Ni(II) complexes may exist under certain conditions although evidence is at present lacking in the form of X-ray structural determinations on any four-coördinate paramagnetic Ni(II) complex.

Ligand field theory easily shows the possible existence of planar spin-free Ni(II) complexes. It is seen in Fig. 1 that a field of D_{4h} symmetry decomposes the free ion states into A, B and E orbital states, some of which can be correlated with those states arising from the direct products of the only strong field configurations which need to be considered here, *viz.*, $a_{1g}^2\ e_g^4\ b_{2g}^2$, $b_{2g}^1b_{1g}^1$, b_{1g}^2. There exists a spin discontinuity in the ground state at some critical value λ of the ligand field strength so that the complex will be spin-free or spin-paired depending on the strength of the field imposed by the four donor atoms. Energy level diagrams of Ni(II) in tetragonal, *cis*- and *trans*-planar symmetries have been elaborately derived by Maki[21] and show the existence of ground state spin changes in each case.

An early compilation of magnetic data for Ni(II) complexes[22] plus more recent observations reveal that all Ni–O_4 type complexes are paramagnetic[22a] whereas Ni–S_4 and Ni–S_2N_2 complexes are diamagnetic (in the absence of steric strain). With Ni–N_4 and Ni–O_2N_2 complexes there is a distribution, by far most prevalent in the latter case, between spin-paired and spin-free forms depending on the specific nature of the ligand donors within a class and the additional factors of solvent and temperature.[17] While such a classification must be accepted with some reservation, it does present a picture consistent with a planar structure for compounds so classified, for nitrogen is known to produce a ligand field splitting greater than oxygen, and sulfur may exert an influence equivalent to two nitrogens.[23] The Ni–O_2N_2 case at this time seems particularly representative of the intermediate situation in which the ligand field strength may or may not be sufficient to pair spins.[24]

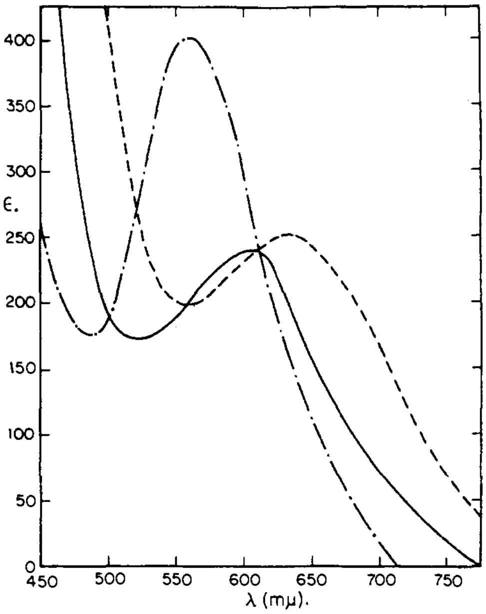

Fig. 2.—Effect of bridge length on ligand field strength—bis-(salicylaldehyde)-diimine Cu(II): —·—·, ethylene; ——, trimethylene; ----, tetramethylene.

It is the intent of this series of investigations to examine spectral and magnetic properties of quadricoördinate Ni(II) complexes in which the ligand field strength is near to that at the ground state cross-over point. It is first necessary to examine ligand field spectra of a series of complexes with fixed stereochemistry in order to determine those factors which allow this point to be approached. For this reason the first series of complexes to be examined is that of the *cis* Ni–O_2N_2 type, derived from the Schiff bases of salicylaldehyde[25] and acetylacetone[26–28] with diamines. Because all of these compounds are diamagnetic solids, the approach is made from the "strong" field side. These ligand systems furnish fields of C_{2v} symmetry and impose a planar or nearly planar stereochemistry on the metal.

Experimental

Preparation of Compounds.—Nearly all the compounds examined were prepared according to previously published methods. All compounds correctly analyzed for metal and nitrogen. References to the original preparations are given below.

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[21] G. Maki, *J. Chem. Phys.*, **28**, 651 (1958).

[22] D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 475 (1940).

[22a] NOTE ADDED IN PROOF.—Recently it has been shown (J. P. Fackler, Jr., and F. A. Cotton, THIS JOURNAL, in press) that certain substituted Ni(II) acetylacetonates are diamagnetic and that the paramagnetism of other such complexes may be due to association rather than being characteristic of the individual molecules.

[23] P. George and D. S. McClure, "Progress in Inorganic Chemistry," Vol. I, Interscience Publishing Co., New York, N. Y., 1959, p 451.

[24] A generally similar situation exists with Co(II) complexes; *cf.* F. A. Cotton and R. H. Holm, THIS JOURNAL, **82**, 2979 (1960).

[25] P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Ann.*, **503**, 84 (1933), and later papers.

[26] P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, THIS JOURNAL, **77**, 5820 (1955).

[27] R. J. Hovey, J. J. O'Connell and A. E. Martell, *ibid.*, **81**, 3189 (1959).

[28] A. E. Martell, R. L. Belford and M. Calvin, *J. Inorg. Nuclear Chem.*, **5**, 170 (1958).

Ligand	Reference Cu	Ni
Bis-(salicylaldehyde)-ethylenediimine	25	25
Bis-(salicylaldehyde)-propylenediimine	25	29
Bis-(salicylaldehyde)-trimethylenediimine	25	[a]
Bis-(salicylaldehyde)-tetramethylenediimine	25	[a]
Bis-(salicylaldehyde)-*o*-phenylenediimine	25	30
Bis-(acetylacetone)-ethylenediimine	26	26
Bis-(acetylacetone)-propylenediimine	26	26
Bis-(acetylacetone)-trimethylenediimine	26	[a]
Bis-(trifluoroacetylacetone)-ethylenediimine	26	[a]
Bis-(trifluoroacetylacetone)-propylenediimine	26	27
Bis-(trifluoroacetylacetone)-trimethylenediimine	28	[b]
Bis-(benzoylacetone)-ethylenediimine	26	26
Bis-(benzoylacetone)-trimethylenediimine	26	[b]
Bis-(benzoylacetone)-tetramethylenediimine	27	[b]
Bis-(formylcamphor)-ethylenediimine	31	31

[a] See preparation directions below. [b] No complex could be isolated.

References to preparation of Cu(II)–diketone complexes are given in Table III. The author is indebted to Mr. J. P. Fackler, Jr., of M.I.T. for the loan of several of these complexes.

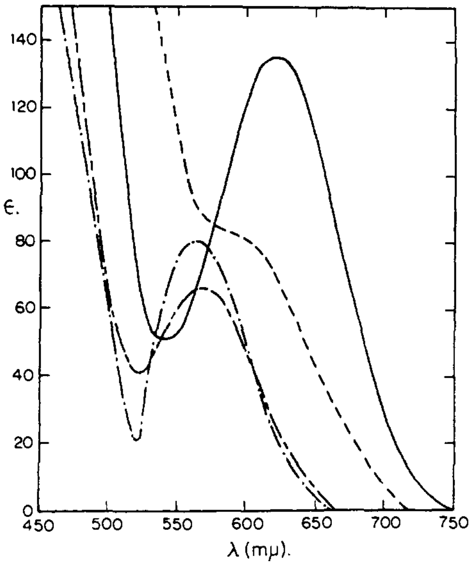

Fig. 3.—Visible spectra of Ni(II) complexes: —.—., bis-(acetylacetone)-ethylenediimine; — — — —, bis-(trifluoroacetylacetone)-ethylenediimine; - - - - - -, bis-(salicylaldehyde)-trimethylenediimine; ———, bis-(formylcamphor)-ethylenediimine.

Bis-(salicylaldehyde)-trimethylenediimine Ni(II).—2.0 g. (0.006 mole) of bis-(salicylaldehyde) Ni(II) dihydrate was slurried with 15 ml. of ethanol. 0.60 g. (0.008 mole) of trimethylenediamine was added and the mixture refluxed for 2 hr. 100 ml. of ethanol was then added, the solution was heated to near boiling, filtered and cooled in ice. Brown needle-like crystals were formed. This product was recrystallized twice from 95% ethanol and air-dried. A second crop was obtained by concentrating the mother liquor.

Anal. Calcd. for $NiC_{17}H_{16}O_2N_2$: Ni, 17.31; C, 60.23; H, 4.76; N, 8.26. Found: Ni, 17.3; C, 60.62; H, 4.68; N, 8.33.

If a greater than two-fold mole excess of diamine was used, a second product was isolated having the composition $NiC_{20}H_{26}O_2N_4$.

Anal. Calcd: Ni, 14.20; C, 58.12; H, 6.34; N, 13.56. Found: Ni, 14.2; C, 57.34; H, 6.45; N, 13.76.

This compound, now being investigated, may be a simple adduct coördinating through one nitrogen or the complex derived from a 1:1 molar condensation of the salicylaldehyde and diamine.

Bis-(salicylaldehyde)-tetramethylenediimine Ni(II).—Bis-(salicylaldehyde) Ni(II)·2H₂O and the diamine in 1.5/1 mole proportions were slurried in ethanol and heated on the steam-bath with stirring for ~40 min. The bright green product was filtered off, washed well with alcohol and acetone and dried *in vacuo*.

Anal. Calcd. for $NiC_{18}H_{18}O_2N_2$: Ni, 16.62; C, 61.24; H, 5.14; N, 7.94. Found: Ni, 16.4; C, 60.89; H, 5.37; N, 8.17.

Bis-(acetylacetone)-trimethylenediimine Ni(II).—2 g. (0.0021 mole) of freshly precipitated and washed $Ni(OH)_2$ was refluxed with 4.8 g. (0.0021 mole) of the Schiff base[26] in 25 ml. of acetone. After a few minutes a blue product began to form. Refluxing continued for 2 hr., the product filtered off and re-crystallized three times from chloroform. 1.0 g. of blue crystals isolated. Analysis and infrared spectrum showed this product to be the dihydrate.

Anal. Calcd. for $NiC_{13}H_{20}O_2N_2 \cdot 2H_2O$: Ni, 17.73; C, 47.17; H, 7.31; N, 8.46. Found: Ni, 17.5; C, 47.46; H, 7.28; N, 8.70.

The water could not be removed by heating *in vacuo* at 150°.

Bis-(trifluoroacetylacetone)-ethylenediimine Ni(II).—The compound was obtained by direct reaction of the Schiff base[26] with nickel acetate in ethanol. The filtered product was washed well with hot ethanol and air-dried. Rust-brown fibrous crystals were obtained.

Anal. Calcd. for $NiC_{12}H_{12}O_2N_2F_6$: Ni, 15.09; C, 37.06; H, 3.11; N, 7.20. Found: Ni, 15.0; C, 37.19; H, 3.32; N, 7.03.

Spectra.—All spectra were obtained at room temperature on a Cary Model 11 recording spectrophotometer with quartz cells.

Discussion

Spectral data in solution for Ni(II) and Cu(II) Schiff base complexes are given in Tables I and II. The Cu(II) complexes were included with the hope of providing an independent measure of the field strengths manifested by the various ligand systems. Monomeric cupric complexes are of course always paramagnetic regardless of field strength and, except for a covalency correction,[32] should reflect the relative order of ligand field strengths expected in the corresponding Ni(II) complexes. The spectra of a number of the cupric complexes have been reported previously,[28] but because of small differences in λ_{max} and for the sake of a more direct comparison in this and future work, new data are given here. Diamagnetic Ni(II) complexes in C_{2v} symmetry exhibit only one spin-allowed band in the visible region (Fig. 3). This has been assigned as the $^1A_1(F) \rightarrow {}^1B_1(G)$ transition.[33] With one exception the data indicate that with an ethylene bridge all Ni(II) complexes absorb in the approximate range 535–570 mμ. With the acetylacetone–diimine complexes red shifts can be effected, as with the analogous Cu(II) complexes of diketones[34] and Schiff bases,[28] by the introduction of a $-CF_3$ group, but the field weakening is quite small. The data (Tables I and III) show that the substituent effects are generally the same in Cu(II) diketone and Schiff base complexes. A number of substituted β-diketone Cu(II) complexes were investigated, but no large red shifts

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(29) P. Pfeiffer, *et al.*, *J. prakt. chem.*, **149**, 217 (1937).

(30) P. Pfeiffer, *et al.*, *ibid.*, **149**, 15 (1937).

(31) P. Pfeiffer, *et al.*, *ibid.*, **150**, 261 (1938).

(32) J. Owen, *Discussions Faraday Soc.*, **19**, 127 (1955); *Proc. Roy. Soc.* (*London*), **A227**, 183 (1955).

(33) G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).

(34) R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

TABLE I

VISIBLE SPECTRAL DATA FOR ACETYLACETONE–DIIMINE COMPLEXES IN CHLOROFORM

			Cu complexes			Ni complexes		
			λ_{max}			λ_{max}		
R[a]	R'[b]	B[c]	mμ	cm.$^{-1}$	ε	mμ	cm.$^{-1}$	ε
CH_3	CH_3	$(CH_2)_2$	540	18,520	198	565	17,700	80
CF_3	CH_3	$(CH_2)_2$	553	18,080	160	572	17,480	63
CH_3	CH_3	$CH_2C(CH_3)H$	540	18,520	203	562	17,790	72
CF_3	CH_3	$CH_2C(CH_3)H$	..	....	..	568	17,610	59
CH_3	CH_3	$(CH_2)_3$	590	16,950	133	587[d]	17,040[d]	46[d]
CF_3	CH_3	$(CH_2)_3$	605	16,530	113	..	....	..
CH_3	C_6H_5	$(CH_2)_2$	545	18,350	260	562	17,790	174
CH_3	C_6H_5	$(CH_2)_3$	604	16,560	133	..	....	..
CH_3	C_6H_5	$(CH_2)_4$	632	15,820	165	..	....	..

[a] Group attached to carbonyl carbon. [b] Group attached to imine carbon. These positions have been assigned from dipole moment studies; *cf.* P. J. McCarthy and A. E. Martell, THIS JOURNAL, **78**, 264 (1956), and also ref. 37. [c] Bridging group. [d] Data refer to the dihydrate. This compound is a paramagnetic solid so that these data are not to be compared with other data in the table.

TABLE II

VISIBLE SPECTRAL DATA FOR SALICYLALDEHYDE–DIIMINE COMPLEXES IN CHLOROFORM

	Cu			Ni		
	λ_{max}			λ_{max}		
B[a]	mμ	cm.$^{-1}$	ε	mμ	cm.$^{-1}$	ε
$(CH_2)_2$	560	17,860	400	540[b]	18,520[b]	140[b]
$CH_2C(CH_3)H$	560	17,860	400	535[b]	18,690[b]	130[b]
o-C_6H_4	570[b]	17,540[b]	350[b]	570–585[b]	.....	..
$(CH_2)_3$	603	16,580	240	595[b]	16,800[b]	80[b]
$(CH_2)_4$	638	15,670	260	600–630[c]	.....	..
Bis-(formylcamphor)-ethylenediimine	552	18,120	320	622	16,080	138
	703	14,220	90			

[a] Bridging group. [b] Approximate values (λ ± 10 mμ, ε ± 20) absorptions appear as shoulders on more intense energy bands. [c] Saturated solution used, band broad and poorly defined.

TABLE III

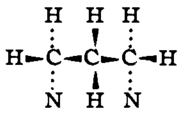
VISIBLE SPECTRAL DATA FOR SUBSTITUTED Cu(II) ACETYLACETONATE COMPLEXES IN CHLOROFORM

				λ_{max}		
R	R'	R''[g]	Ref.	mμ	cm.$^{-1}$	
CH_3	CH_3	H	[a]	650	15,380	38
CH_3	CH_3	CH_3	[b]	643	15,550	41
CH_3	CH_3	Cl	[c]	650	15,380	40
CH_3	CH_3	NO_2	[d]	652	15,340	45
CF_3	CH_3	H	[a]	665	15,040	37
C_2F_5	CH_3	H	[e]	663	15,080	38
C_3F_7	CH_3	H	[e]	660	15,150	41
CH_3	C_6H_5	H	[b]	650	15,380	45
CF_3	C_6H_5	H	[f]	664	15,060	43
CF_3	CF_3	H	[a]	680	14,710	38
C_6H_5	C_6H_5	H	[b]	645	15,500	[h]
Bis-(salicylaldehyde) Cu(II)				670	14,930	69

[a] Ref. 34. [b] H. F. Holtzclaw, Jr., K. W. R. Johnson and F. W. Hengeveld, THIS JOURNAL, **74**, 3776 (1952). [c] H. F. Holtzclaw, Jr. and J. P. Collman, *ibid.*, **79**, 3318 (1957). [d] C. Djordjevic, J. Lewis and R. S. Nyholm, *Chem. and Ind.* (London), 122 (1959). [e] J. D. Park, H. A. Brown and J. R. Lacher, THIS JOURNAL, **75**, 4753 (1953). [f] J. C. Reid and M. Calvin, *ibid.*, **72**, 2948 (1950). [g] Group attached to unique carbon of the chelate ring. [h] Saturated solution.

were observed except in bis-(hexafluoroacetylacetonato) Cu(II),[34] and, as previously noted,[28] the diketone failed to form the desired Schiff bases.

The only significant decrease in the apparent ligand field strength is that brought about by the introduction of a tri- or tetramethylene bridge (Figs. 2 and 3). The effect of the trimethylene bridge was first observed by Martell, Belford, and Calvin[28] in two acetylacetone–diimine cupric complexes. The same effect is present in the Ni(II) complexes of salicylaldehydetrimethylenediimine, causing a red shift of 1700 cm.$^{-1}$ relative to the ethylene compound. This is far greater than any substituent effect, but bis-(salicylaldehyde)-trimethylenedimine Ni(II) was found to be diamagnetic and to possess the characteristic spectrum of these diamagnetic compounds.[35] The source of the decrease in field intensity is not clear. Two conformations of the bridge, both of C_{2v} symmetry, which allow the $Ni–O_2N_2$ grouping to remain planar can be visualized. In I non-bonded repulsions are minimized and the N–N distance, assuming normal bond parameters,[36] is 2.5 Å., leading to an essentially strain-free configuration and comparing favorably with intramolecular O–N distances (2.5, 2.7 Å.) in bis-(salicylaldimine) Ni(II)[7] and the N–N distance (2.5 Å.) in bis-(salicylaldehyde)-ethylenediimine Co(II).[36] II represents rotation about the C–C bonds by 55° and produces an N–N distance of ~3.5 Å., this configuration could decrease the metal–nitrogen distances thereby weakening the field. Certainly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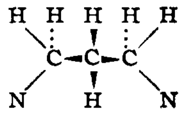
II

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[35] Bis-(salicylaldehyde)-trimethylenediimine Ni(II), apparently anhydrous, has been reported to be paramagnetic with a moment of 3.3 B.M. (C. H. Barkelew, Ph.D. Thesis, University of California, Berkeley, 1944). The anhydrous penta- (R. W. Asmussen, Thesis, Copenhagen, 1944) and tetra- and hexamethylene (Barkelew, above) homologs are diamagnetic.

[36] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 266.

there is no profound geometric change in going from the ethylene to the trimethylene derivatives, as is borne out by the dipole moment data of McCarthy and Martell[37] who find a difference of ~0.3 D. in two such instances. The effect of non-planarity of the $M{-}O_2N_2$ system on the absorption spectrum is not easily assessed. The chelate rings in bis-(acetylacetone)-*cis*-1,2-hexanediimine Cu(II) and Ni(II) are considered to be non-planar,[38] but no important spectral differences in solution compared to the ethylene analogs were observed. Introduction of a tetramethylene bridge produces even larger red shifts and band broadenings, but bis-(salicylaldehyde)-tetramethylenediimine Ni(II) and its higher homologs are diamagnetic though not necessarily strictly planar.[39]

The Ni(II) complex of bis-(formylcamphor)-ethylenediimine possesses the weakest ligand field of any of the nickel complexes, yet contains a two-carbon bridge. Again, the cause of this field weakening is not clear but the position of λ_{max} is relevant to the remarkable magnetic behavior of this complex in solution. Bis-(formylcamphor)-ethylenediimine Ni(II), diamagnetic as a solid, becomes partially paramagnetic in benzene, methylbenzenes and methanol yet is diamagnetic in chloroform and pyridine[17]; bis-(acetylacetone)-ethylenediimine Ni(II) is diamagnetic in chloroform and ethanol.[17] Diamagnetic solid bis-(salicylaldoxime) and bis-(N-methylsalicylaldimine) Ni(II) have λ_{max} in chloroform in the range 610–620 mμ[18,33] and manifest partial paramagnetism in chloroform and benzene, becoming fully paramagnetic in pyridine.[17,18]

If an average ligand field of tetragonal symmetry may be assumed, then the strength of this average field must be very near that at the magnetic cross-over point and small perturbations of field strength, such as the introduction of a weak tetragonal z-component by solvation or association and the removal of intermolecular crystalline fields. are sufficient to decrease the singlet-triplet separation.[33] This is in keeping with Maki's result that as the in-plane components of the ligand field are decreased a smaller axial component is required for partial paramagnetism.[33] The spectral data (Tables I and II) indicate that for *cis*-planar complexes the ligand field is stronger than that in *trans*-planar complexes with apparently equivalent sets of donor atoms, and for this reason stabilization of a triplet state is more difficult to achieve.

Temperature dependent magnetic studies of the *cis*- and *trans*-planar cases in solution are underway.

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[38] M. Honda and G. Schwarzenbach, *Helv. Chim. Acta*, **40**, 27 (1957).

[39] Recently a diamagnetic tetracoördinate Ni(II) complex has been partially resolved; *cf.* H. Irving and J. B. Gill, *Proc. Chem. Soc.*, 168 (1958); H. Irving, J. B. Gill, W. R. Cross, *J. Chem. Soc.*, 2087 (1960).

[CONTRIBUTION FROM THE DIVISION OF SCIENCES, LOUISIANA STATE UNIVERSITY IN NEW ORLEANS, LAKE FRONT, NEW ORLEANS, LOUISIANA]

Extraction of Group VIII Metals by Long Chain Alkyl Amines. I. A Tracer Study of Iron(III)–Chloride Systems[1]

BY MARY L. GOOD AND SARA E. BRYAN

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The distribution of Fe(III) between aqueous hydrochloric acid solutions and various long chain alkyl amines in organic solvents has been investigated using tracer techniques. The effects of HCl concentration, structure of the amine, and type of organic solvent have been extensively studied. The extracted Fe(III) species in the organic phase has been observed spectrophotometrically and evidence is presented to support the conclusion that the extracted species is the tetrachloroferrate(III) ion.

Introduction

The use of alkyl amines as liquid extractants for various anionic species of metal ions has been largely confined to the separation of a few scattered pairs of metal ions[2–5] and to the extraction of uranium, thorium and plutonium.[6–9] In most analytical separations and purifications reported, the successful procedures were determined empirically for the particular system under study. However, some work has been done using the extraction information to elucidate the structures of the anionic species, particularly for uranyl sulfate and ferric sulfate complexes.[10–12] Also, some of the work done at the Oak Ridge National Laboratory has been accumulated and compared, showing that many fac-

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