sorption curve for the phen complex begins to follow that of the ligand. The curve of the iron complex does not coincide with that of dipy until about 32,000 cm.$^{-1}$. Thus the absorption of the phen complex in the region of 29,000 cm.$^{-1}$ is almost identical with that of the ligand, but the same is not true for the dipy complex. A change in dipy as a result of coordination is suggested. In solution the benzene rings are not in fixed positions for dipy and solvation should favor a *trans* arrangement. On coordination to a metal ion the two rings must become approximately coplanar with the N atoms in *cis* positions. It is suggested that the 28,600 cm.$^{-1}$ band of [Fe(dipy)$_3$]$^{2+}$ is associated with this change in the symmetry of the ligand. This would permit new transitions involving the π-system of dipy, similar to those of phen.

The great similarity among the intense CD bands of opposite sign in the ultraviolet region for all of the dipy and phen complexes provides a means of relating the configurations of these complexes. The (+)$_{589}$-[Fe(phen)$_3$](ClO$_4$)$_2$, (+)$_{589}$-[Fe(dipy)$_3$](ClO$_4$)$_2$, and (−)$_{546}$-[Ni(dipy)$_3$](ClO$_4$)$_2$ all have the same sign pattern for the dominant CD peaks and hence are concluded to have the same configuration. The reversed sign pattern of (+)$_{589}$-[Ni(phen)$_3$](ClO$_4$)$_2$ indicates that this complex has the opposite configuration. Presumably the configuration of (−)$_{589}$-[Co(en)$_2$phen]I$_3$ is the same as that of (+)$_{589}$-[Ni(phen)$_3$](ClO$_4$)$_2$, although data are not available for the expected higher frequency component of the Co(III) complex.

Mason[2] reported the CD curve for (−)-[Ru(phen)$_3$](ClO$_4$)$_2$ which is very similar to that for (+)$_{589}$-[Fe-(phen)$_3$](ClO$_4$)$_2$ except that the signs of the major CD peaks in the low frequency region are reversed. This reversal of signs in one region is surprising in view of the consistency among the complexes reported here. Mason assigned the intense negative band of the CD curve in the main ligand band region as an A$_2$ component and the positive band as one with E symmetry. He stated that since the A$_2$ component was negative the complex consisted of a left-handed helix, the same as Λ-[Co(en)$_3$]$^{3+}$. If Mason's assignment is correct the Λ configuration can be assigned to (+)$_{589}$-[Fe(phen)$_3$]-(ClO$_4$)$_2$, (+)$_{589}$-[Fe(dipy)$_3$](ClO$_4$)$_2$, and (−)$_{546}$-[Ni(dipy)$_3$](ClO$_4$)$_2$ and the Δ configuration to (+)$_{589}$-[Ni(phen)$_3$](ClO$_4$)$_2$ and tentatively to (−)$_{589}$-[Co(en)$_2$phen]I$_3$.

The solubilities of diastereoisomers have been used to assign the relative configurations of complexes. Even though the antimonyl *d*-tartrate ion was used for the resolution of the tris(phen) and tris(dipy) complexes, the resulting diastereoisomers differ in composition[18] and hence the solubility rule would not be expected to relate the configurations of the phen complexes to the dipy complexes. The solubility rule should be valid for relating the configurations of the phen complexes of Fe(II) and Ni(II) and (separately) the dipy complexes of Fe(II) and Ni(II). The results are consistent with the assignment made based on the CD data. The phen complex of each metal which gives the less soluble diastereoisomer is Δ and the dipy complex of each metal which gives the less soluble diastereoisomer is Λ.

(18) F. P. Dwyer and E. C. Gyarfas[14] established the compositions of the Fe(II) compounds as [Fe(dipy)$_3$]$_5$(SbOC$_4$H$_4$O$_6$)$_4$I$_2$·18H$_2$O and [Fe(phen)$_3$]-(SbOC$_4$H$_4$O$_6$)$_2$·4H$_2$O.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY, SYRACUSE, NEW YORK 13210

Magnetic Properties of Some High-Spin Complexes of Iron(II)

BY W. A. BAKER, JR., AND H. M. BOBONICH

The magnetic susceptibilities of several high-spin complexes of Fe(II) having the general formula [Fe(phen)$_2$X$_2$] (phen = 1,10-phenanthroline; X$^-$ = Cl$^-$, Br$^-$, I$^-$, N$_3$$^-$, SCN$^-$, SeCN$^-$) were determined over the temperature range 100–300°K. The moments found are somewhat lower than those expected for rigorously octahedral complexes and are essentially independent of temperature, except for the thiocyanate and selenocyanate, in which the moment is found to decrease sharply from ~5.0 to ~1.5 B.M. at lower temperatures. Structures are proposed for these complexes, based on X-ray and infrared data.

A series of Fe(II) complexes having the general formula [Fe(phen)$_2$X$_2$] (hereafter referred to as the bis complexes; phen = 1,10-phenanthroline) have recently been prepared and their magnetic moments at room temperature reported.[1-3] In all cases, the room temperature moments observed, 5.1–5.3 B.M., are somewhat below that predicted for octahedral, spin-free, d^6 systems when spin–orbit coupling is included.[4,5] This lowering of the moments is at least in part a result of the fact that, in the complexes studied, the symmetry is not truly cubic due to the difference in ligand field strength between phen and X. Thus the moment is partially quenched by the lower symmetry.

Since very little work has been done on the tempera-

(1) F. Basolo and F. P. Dwyer, *J. Am. Chem. Soc.*, **76**, 1454 (1954).
(2) K. Madeja and E. Konig, *J. Inorg. Nucl. Chem.*, **25**, 377 (1963).
(3) W. A. Baker, Jr., and H. M. Bobonich. *Inorg. Chem.*, **2**, 1071 (1963).
(4) J. S. Griffith, *Trans. Faraday Soc.*, **54**, 1109 (1958).
(5) B. N. Figgis, *Nature*, **182**, 1568 (1958).

ture dependence of the susceptibilities of high-spin d^6 systems except for a variety of hydrated Fe(II) salts[6] and several salts of $CoF_6{}^{3-}$,[7] we felt it would be interesting to measure the temperature dependence of a variety of bis complexes. This is part of a general effort to determine in more detail the effects of low symmetries on magnetic and spectral properties of coordination compounds.

Experimental

Materials.—[Fe(phen)$_2$X$_2$] (X$^-$ = Cl$^-$, Br$^-$, I$^-$, SCN$^-$) were prepared as previously described.[3]

[Fe(phen)$_2$(N$_3$)$_2$].—The bis azide was prepared by suspending [Fe(phen)$_3$](N$_3$)$_2$ in methylcyclohexane and refluxing for 7 hr. *Anal.* Calcd. for Fe(C$_{24}$H$_{16}$N$_4$)(N$_3$)$_2$: C, 57.62; H, 3.22; N, 28.00. Found: C, 56.92; H, 2.95; N, 27.10.

[Fe(phen)$_2$(SeCN)$_2$].—The bis selenocyanate was prepared by heating [Fe(phen)$_3$](SeCN)$_2$ *in vacuo* at 163° for 5 days. *Anal.* Calcd. for Fe(C$_{24}$H$_{16}$N$_4$)(SeCN)$_2$: C, 49.86; H, 2.58; N, 13.42. Found: C, 50.08; H, 2.58; N, 13.22.

[Fe(bipy)$_2$(SCN)$_2$].—The preparation of [Fe(bipy)$_2$(SCN)$_2$] (bipy = 2,2'-bipyridyl) was accomplished by suspending [Fe(bipy)$_3$](SCN)$_2$ in methylcyclohexane and refluxing for 103 hr. The suspended material was filtered, washed, and then suspended in toluene and refluxed for 5 hr. *Anal.* Calcd. for Fe(C$_{20}$H$_{16}$N$_4$)(SCN)$_2$: C, 54.55; H, 3.33; N, 17.35. Found: C, 54.34; H, 3.25; N, 17.22.

Magnetic Measurements.—Susceptibilities were obtained using a standard Gouy balance, utilizing a Varian 4-in. electromagnet with associated current regulator and power supply and a Mettler H-16 semimicrobalance. All measurements were made at three field strengths (3.0, 4.5, and 6.6 kgauss), and no field dependence was observed. Diamagnetic corrections were made using values given by Figgis and Lewis.[8] The magnetic moment, μ, was obtained from the relationship $\mu = 2.84[\chi_M{}^{cor} \cdot (T - \theta)]^{1/2}$ when θ was evaluated and $\mu = 2.84(\chi_M{}^{cor} T)^{1/2}$ otherwise.

Infrared Spectra.—All infrared spectra were obtained using a Perkin-Elmer Model 521 grating spectrometer. The KBr pellet technique was used for sample preparation.

X-Ray Powder Data.—X-Ray data were obtained using a G.E. diffraction unit and a Norelco powder camera of 57.3-mm. radius. Cu Kα radiation and a Ni filter were used. Results were recorded photographically and the relative intensities were estimated visually. The low temperatures were obtained by blowing He, which had been cooled by passing through a coil immersed in liquid N$_2$, over the sample. A thermocouple was located near the sample for temperature measurements.

Microanalyses.—Analyses of C, H, and N were performed by the Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

Magnetic Data.—The magnetic data for the bis complexes are given in Table I and in part in Fig. 1. It is obvious from inspection of the data that the complexes studied fall into two classes. For the Cl$^-$, Br$^-$, I$^-$, and N$_3{}^-$ complexes, the moments are $\sim$5.0 B.M. and essentially independent of temperature. For the SCN$^-$ and SeCN$^-$ complexes, the moments are observed to drop sharply from $\sim$5.0 to $\sim$1.5 B.M. at lower temperatures.

(6) G. Föex, C. J. Gorter, and L. J. Smits, "Constants Sélectionnées Diamagnetisme et Paramagnetisme," Masson et Cie, Paris, 1957.

(7) F. A. Cotton and M. D. Myers, *J. Am. Chem. Soc.*, **82**, 5023 (1960).

(8) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York N. Y. 1960.
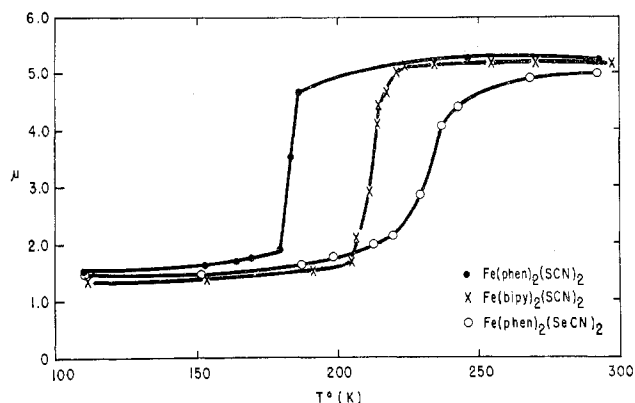
TABLE I

MAGNETIC DATA FOR [Fe(phen)$_2$X$_2$] AND [Fe(bipy)$_2$(SCN)$_2$]

Compound	Temp., °K.	$\chi_M{}^{cor} \times 10^6$	μ, B.M.
[Fe(phen)$_2$Cl$_2$]	291	11,818	5.27
($\theta = 0$°K.)	245	14,211	5.30
	187	18,250	5.25
	152	22,064	5.21
	111	31,189	5.28
[Fe(phen)$_2$Br$_2$]	295	10,938	5.15
($\theta = -6$°K.)	248	13,341	5.23
	188	17,068	5.17
	154	20,594	5.15
	111	29,063	5.23
[Fe(phen)$_2$I$_2$]	294	10,798	5.13
($\theta = -8$°K.)	249	12,802	5.15
	189	16,260	5.08
	154	19,483	5.04
	111	27,310	5.11
[Fe(phen)$_2$(N$_3$)$_2$]	295	11,182	5.14
($\theta = +2$°K.)	245	13,864	5.21
	185	17,966	5.15
	152	21,489	5.10
	110	30,379	5.15
[Fe(phen)$_2$(SCN)$_2$]	293	11,518	5.22
	246	13,866	5.25
	186	14,201	4.62
	183	8,376	3.52
	179	2,514	1.90
	169	2,216	1.74
	164	2,189	1.70
	153	2,125	1.62
	110	2,690	1.54
[Fe(phen)$_2$(SeCN)$_2$]	292	10,563	4.99
	268	11,159	4.91
	242	9,762	4.37
	236	8,729	4.08
	230	4,333	2.83
	219	2,773	2.21
	212	2,260	1.97
	198	1,928	1.76
	186	1,727	1.61
	151	1,790	1.48
	110	2,398	1.46
[Fe(bipy)$_2$(SCN)$_2$]	297	11,068	5.15
	270	12,351	5.19
	254	13,063	5.18
	235	14,052	5.16
	224	14,551	5.12
	221	14,066	5.01
	217	12,351	4.65
	215	10,196	4.20
	213	9,832	4.11
	211	4,955	2.90
	206	2,576	2.07
	205	1,564	1.61
	191	1,467	1.50
	153	1,564	1.39
	112	2,048	1.36

There are several points of interest in regard to these data. There is first the fact that the largest moment observed is 5.3 B.M., for the chloride. Using the results obtained by Figgis[5] and the free-ion value of 100 cm.$^{-1}$ for the spin–orbit coupling constant, one would expect a room temperature moment of $\sim$5.6 B.M., increasing monotonically to $\sim$5.75 at 150°K. and decreasing thereafter. From the results given in

Fig. 1.—Magnetic moment *vs.* temperature for the thiocyanate and selenocyanate complexes.

Table I, the room temperature moments are in the order $I^- < N_3^- < Br^- < SCN^- < Cl^-$. The $SeCN^-$ complex is omitted since it appears from the data that whatever the effect that is responsible for the drastic drop in moment, it is already becoming important near room temperature. Since the order attained is essentially the same as the order of the ligands in the spectrochemical series, the lowered moment (below that expected from theory) is at least partly due to the fact that the complexes studied deviate appreciably from pure cubic symmetry, and the weaker the ligand field strength of X^-, the more the asymmetry and the lower the moment. The lowering of the moment arises from the fact that the $^5T_{2g}$ state of the octahedral complex splits[9] into "nonmagnetic" A and E states under the influence of the asymmetry. Delocalization of metal d-electrons onto the ligands might also be a factor in the lowering of the moment.

The second point that must be considered is the temperature dependence of the moment. For the Cl^-, Br^-, I^-, and N_3^- complexes there is a slight trend, although not a monotonic one, to lowered moments at lower temperatures. This behavior is again a reflection of the asymmetry, which will be more important at lower temperatures, and thus offsets the expected increase due to spin–orbit coupling. It is worth pointing out that, in all cases, the moments do rise slightly to maxima at $\sim250°$ and, for the "normal" complexes, drop slightly to minima at $\sim150°$ and rise again at $\sim110°$. We cannot interpret these variations, but, after a careful study of the data and an evaluation of experimental errors involved, we believe that the effects are real ones. The results seem to indicate a balance between the tendency of spin–orbit coupling to increase and the asymmetric fields to decrease the moment as the temperature is lowered.

There is also a slight contribution to the moment to be expected from the "mixing in" of higher levels due to spin–orbit coupling.[5] The exact magnitude of this effect cannot be evaluated and it has been neglected, but it should not affect the conclusions drawn.

The most interesting and unfortunately the most puzzling data are those for the SCN^- and $SeCN^-$

complexes. The sudden drop in moment below $200°$ is to our knowledge unique. The effect vaguely resembles antiferromagnetism, but the decrease in moment is much sharper than that usually observed. Gradual decreases in moment, however, have been observed for a variety of polynuclear complexes,[10] so this structural possibility was suggested. This topic is developed more fully in the following sections.

Conductance Data.—In an effort to gain more information to assist in interpreting the magnetic data, attempts were made to obtain conductance data on the bis complexes. Altogether, approximately 30 solvents were used. In any solvent in which the complexes were sufficiently soluble for measurement, they also decomposed to give $[Fe(phen)_3]^{2+}$, which was identified by its visible absorption spectrum. The decomposition was extremely rapid and easily observed since the bis complexes are deep blue and $[Fe(phen)_3]^{2+}$ is red. No attempt was made to identify the other products of the decomposition.

X-Ray Data.—The X-ray data as obtained from powder photographs yield information which aids in interpreting the magnetic data. The data for the SCN^- and $SeCN^-$ complexes are given in Table II. The data were obtained at room temperature and at a temperature below that at which the magnetic moment drops to its low value. It is clear from a comparison of the data obtained at the two temperatures that no structural change occurs as the temperature is lowered, thus ruling out this possibility as an explanation for the unusual magnetic behavior.

Further, an examination of the X-ray data for the Cl^-, Br^-, I^-, and N_3^- complexes shows definite points of similarity between these four complexes that are missing for the magnetically anomalous ones. For example, the four "normal" complexes all show the following lines: one of relative intensity 100 in the range 8.0–8.6 Å.; relative intensity ~70 in the range 7.0–7.2 Å.; relative intensity ~60 in the range 3.9–4.1 Å.; relative intensity ~60 in the range 3.5–3.7 Å.

Visual examination of the films is even more convincing. The "normal" complexes have patterns that are similar to each other but different from the SCN^- and $SeCN^-$ complexes. Furthermore, the similarities between the SCN^- and $SeCN^-$ complexes are also evident upon visual examination. On this basis, it seems reasonable to conclude that the SCN^- and $SeCN^-$ complexes fit into one structural class while the N_3^-, Cl^-, Br^-, and I^- complexes fit into another. The previously reported CN^- complex[3,11] also appears to fall into this latter class. It has been postulated,[12] on the basis of infrared data, that the cyanide is *cis*, and this, if true, would indicate that the other normal bis complexes are also *cis*.

Infrared Data.—There has recently become available a large amount of infrared data (mostly CN stretching

(9) J. H. Van Vleck, *Discussions Faraday Soc.*, **26**, 96 (1958).

(10) A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961).

(11) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

(12) N. K. Hamer and L. E. Orgel, *Nature*, **190**, 439 (1961).

TABLE II

X-RAY DATA ON [Fe(phen)₂(SCN)₂], [Fe(phen)₂(SeCN)₂], AND [Fe(bipy)₂(SCN)₂] AT ROOM TEMPERATURE AND BELOW THE MAGNETIC TRANSITION POINT[a]

[Fe(phen)₂(SCN)₂]

Room temp.		158°K.	
d, Å.	I/I_0	d, Å.	I/I_0
8.68	40	8.82	20
8.02	30	8.17	30
7.31	60	7.36	40
5.90	10	5.90	10
4.69	50	4.67	40
3.81	100	3.82	100
3.30	30	3.28	20
3.20	20	3.20	10
2.61	20	2.60	20
2.17	20	2.15	30

[Fe(phen)₂(SeCN)₂]

Room temp.		160°K.	
d, Å.	I/I_0	d, Å.	I/I_0
7.38	20	7.30	20
5.98	20	5.94	20
5.12	10	5.13	10
4.74	50	4.65	20
3.87	100	3.86	100
3.46	10	3.44	10
3.24	20	3.22	20
2.28	10	2.29	10
2.21	10	2.18	10

[Fe(bipy)₂(SCN)₂]

Room temp.		160°K.	
d, Å.	I/I_0	d, Å.	I/I_0
8.56	60	8.51	50
7.96	60	8.07	50
6.60	20	6.73	25
5.84	30	5.84	25
4.44	50	4.47	15
3.93	100	3.95	100
3.80	20	3.81	10
3.49	20	3.49	25
2.71	10	2.71	10
2.54	10	2.54	10
2.40	10	2.42	10
2.30	10	2.30	10

[a] Numerous lines of relative intensity <10 have been omitted for brevity. Excellent agreement between the two temperatures is also evident in these weak lines.

Fig. 2.—Proposed structure for [Fe(phen)₂(SCN)₂].

TABLE III

INFRARED DATA ON THIOCYANATE AND SELENOCYANATE COMPLEXES

Compound	ν, cm.$^{-1}$
[Fe(phen)₂(SCN)₂]	2015 (sh), 2062 (s), 2073 (s), 2100 (sh)
[Fe(phen)₂(SeCN)₂]	2015 (sh), 2062 (s), 2073 (s), 2095 (sh)
[Fe(bipy)₂(SCN)₂]	2010 (sh), 2062 (s), 2066 (s), 2100 (sh)
KSeCN	2070[a]
KSCN	2053[b]

[a] Reference 17. [b] Reference 18.

or less and two weaker shoulders on either side of the two strong bands. The exact meaning of these results is not clear. The presence of the several bands would normally be interpreted as indicating more than one type of ligand in the complexes. For the complexes in question, this postulate would only seem reasonable if there were bridging and ionic ligands present. That is, the complexes could be binuclear and of the type [(phen)₂Fe(SCN)₂Fe(phen)₂](SCN)₂. Certainly, the positions of the strong bands are in the range expected for ionic groups. There should also, however, be a strong band around 2100–2150 cm.$^{-1}$ for the bridging groups, if analogy can be made with previous work, and this is not observed. Nevertheless, all of the previous bridged complexes studied have apparently been of the type M₁–SCN–M₂, and we feel that it is probable that the present complexes have sulfur bonded to both iron atoms. Exactly what infrared spectrum would be expected for this type of bridging group is not obvious.

In summary, we feel that the presence of several infrared bands indicates, *but does not prove*, that two types of ligands exist in the SCN⁻ and SeCN⁻ complexes, probably bridging and ionic types. The complexity of the spectra and the lack of agreement with other known complexes preclude unambiguous assignment.

Mössbauer Data.—The Mössbauer spectra were obtained on the SCN⁻ and SeCN⁻ complexes.[19] The important result so far as this work is concerned is that there is no difference in either the isomer shifts or the quadrupole splitting for a given complex above and below the magnetic transition temperature. This indicates that there is no appreciable change in the electron distribution, such as from high-spin to low-spin, around each *individual* iron atom, since such changes

frequencies) on thiocyanate[13-16] and selenocyanate[15] complexes that has aided in assigning structures. Thus, for N-bonded groups, the CN frequency is in the range 2040–2090 cm.$^{-1}$, for S-bonded groups it usually is at higher values, 2070–2120 cm.$^{-1}$, and for –NCS– bridging groups it covers a wide range, perhaps 2090–2200 cm.$^{-1}$. This is to be compared with the values found in KSeCN[17] and KSCN[18] of 2070 and 2053 cm.$^{-1}$, respectively.

The data obtained on three such complexes are given in Table III. It can be seen that in all three cases there are two strong bands separated by 10 cm.$^{-1}$

(13) J. Chatt and L. A. Duncanson, *Nature*, **178**, 997 (1956).

(14) J. Chatt, L. A. Duncanson, F. A. Hart, and P. G. Owston, *ibid.*, **181**, 43 (1958).

(15) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, **1**, 565 (1962).

(16) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

(17) H. W. Morgan, *J. Inorg. Nucl. Chem.*, **16**, 367 (1961).

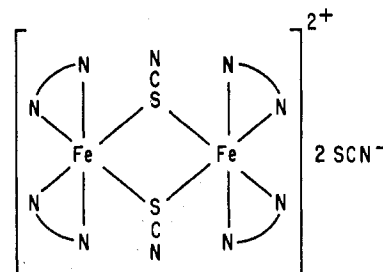(18) L. H. Jones, *J. Chem. Phys.*, **25**, 1069 (1956).

would affect both the isomer shift and the splitting.[20] This lends support to the idea that the lowered moment is a result of interaction between ions.

Structure of the SCN⁻ and SeCN⁻ Complexes.— Based on the evidence presented, the proposed structure for [Fe(phen)₂(SCN)₂] is given in Fig. 2. The structures of [Fe(phen)₂(SeCN)₂] and [Fe(bipy)₂(SCN)₂] are assumed to be analogous. From the X-ray evidence, there is no doubt that these are different in structure from the normal bis complexes. The only explanation for the peculiar magnetic results is one based on ion–ion interaction, although the effects are not similar to those observed for known binuclear complexes[10] and we are unable to explain in more detail the exact nature of the interactions or give a more precise interpretation of the data.[21]

The bridge structure in which either sulfur or selenium is bonded to both atoms is favored over the –NCS– bridge for two reasons. First and most important is the fact that the latter type would place the iron atoms at least 5–7 Å. apart, too far for any strong interactions. On the other hand, in the proposed structure the Fe–Fe distance would certainly be less. There is also the possibility of an indirect interaction through the sulfur in the proposed structure. The second point in favor of the sulfur bridge is the infrared results. This is really negative evidence, since the infrared data indicate the absence of a –NCS– bridge, yet the complexity suggests a complex structure.

(21) It has been pointed out by one of the referees that complexes of higher molecularity cannot be excluded from consideration. We agree, but feel that until more data are available, the binuclear species is most likely.

(20) Unpublished observation. See footnote 19.

# Dielectric Polarization Studies on Cobalt(II) and Cobalt(III) Complexes with Substituted Salicylaldimines[1]

By M. CIAMPOLINI, F. MAGGIO, and F. P. CAVASINO

The molecular polarizations of a number of cobalt(II) and cobalt(III) complexes with substituted salicylaldimines are reported. The values of the electric dipole moments show that the cobalt(III) compounds have the *trans*-octahedral configuration.

Introduction

In recent years diverse complexes of cobalt(III) with N-substituted salicylaldimines of the general formula

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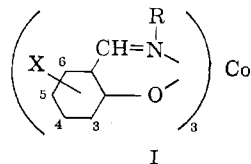
(X = H; R = *n*-alkyl,[2–4] aryl,[2,3] benzyl,[2,3] phenylethyl[2]) have been prepared and studied. The asymmetry of these bidentate ligands makes possible the existence of *cis* and *trans* geometrical isomers of the octahedral cobalt(III) complexes with the configurations
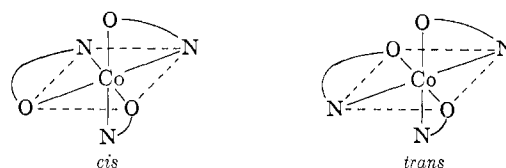
However, only one form was isolated in the solid state.[2,3] On the other hand, the robust character of these complexes,[3] as in general with chelate complexes of cobalt-(III),[5] allows one confidently to exclude the possibility that the form isolated gives in solution at room temperature a mixture of the two geometrical isomers. On the basis of steric considerations[2,3] and the values of the dipole moments,[2] the *trans*-octahedral structure was tentatively assigned to the isolated complexes.

In order definitely to clarify the problem, the dipole moment measurements have been extended to other compounds of cobalt(III) and cobalt(II) with salicylaldimines. Thus, compounds of the type I in which R = *i*-C₃H₇, *n*-C₃H₇; X = 3-Cl, 5-Cl, 3,4-benzo, 5,6-benzo have been prepared and characterized. The dipole moments of all these complexes have been measured.

(1) This work was supported by the U. S. Department of the Army through its European Research Office, under contract No. DA-91-591-EUC-2965, and by the Italian Consiglio Nazionale delle Ricerche.

(2) F. P. Cavasino, M. Ciampolini, and F. Maggio, *Atti Accad. Sci., Lettere Arti Palermo*, **20**, Ser. IV, Pt. I, 5 (1960); *cf. Chem. Abstr.*, **57**, 12,086 (1962).

(3) O. West, *J. Chem. Soc.*, 4944 (1960).

(4) H. Nishikawa, S. Yamada, and R. Tsuchida, *Z. Naturforsch.*, **17b**, 78 (1962).

(5) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **84**, 2303 (1962).