considerably larger than expected for a triplet–singlet transition; the observed absorption maxima occur at higher frequencies than predicted from Liehr and Ballhausen's diagram. However, it has been proposed that this transition may share intensity with a neighboring triplet–triplet transition and be shifted toward it.[11]

Magnetic data for these complexes are summarized in Table III. All compounds have moments falling in the range generally observed for octahedral nickel(II). From these data and Dq, it is possible to calculate values for λ, the spin–orbit coupling constant. These parameters are related by[12]

$$\chi = \frac{8N\beta^2}{3kT}\left(1 - \frac{4\lambda}{10Dq}\right)^2 + \frac{8N\beta^2}{10Dq}$$

It can be seen that λ decreases regularly in magnitude as Dq increases; all compounds have values of λ which are considerably reduced in magnitude from the free ion value of -324 cm.$^{-1}$. Diminishing absolute values of λ have been attributed to covalency.[13] In the complexes under consideration λ increases in absolute value with increasing perchlorate coordination. Certainly, one would assume perchlorato compounds to exhibit appreciable ionic character.

Reduction in B' values has also been attributed to the same cause.[13] While the B' values in these complexes are reduced from that for the free ion (1041 cm.$^{-1}$), they show a different order than do the λ values. It is possible that the B' values are not as reliable an indication of covalent character as are the λ values.

Acknowledgment.—The authors wish to thank the University of Connecticut Research Foundation for partial financial support of this work.

(11) M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, **2**, 1178 (1963).

(12) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p. 142.

(13) J. Owen, *Proc. Roy. Soc.* (London), **A227**, 183 (1955).

CONTRIBUTION FROM THE INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY,
UNIVERSITY OF FLORENCE, FLORENCE, ITALY

Magnetic Investigation of Some Tetracoordinated Nickel(II) and Copper(II) Complexes between 80 and 300°K.[1]

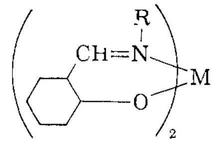
BY L. SACCONI, M. CIAMPOLINI, AND U. CAMPIGLI

Received September 28, 1964

The magnetic susceptibilities between 80 and 300°K. of various N-substituted salicylaldimino complexes of nickel(II) and copper(II) have been measured. The susceptibilities of the distorted tetrahedral complexes of nickel follow the Curie–Weiss law with θ = 9–14°K. and the room-temperature magnetic moments are 3.29–3.34 B.M. The room-temperature moments of the complexes $(R_4N)_2NiX_4$ (X = Cl, Br, I; R = C_2H_5, n-C_3H_7), 3.44–3.89 B.M., are higher and for these 30°K. > θ > 8°K. Some N-aryl salicylaldiminonickel(II) complexes which are probably polymeric with the octahedral structure have room temperature magnetic moments of 3.33–3.39 B.M. and −11°K. > θ > −16°K. The susceptibilities of all copper(II) complexes examined follow the Curie law. The moments of the distorted tetrahedral N-*sec*-alkylsalicylaldiminocopper complexes are slightly larger than those of the N-*n*-alkyl-substituted planar isomers, being 1.90–1.92 and 1.85–1.86 B.M., respectively. The moments of the pseudo-tetrahedral compounds $((C_2H_5)_4N)_2CuX_4$ (X = Cl, Br) are 1.93–1.97 B.M.

Introduction

While it was shown that the complexes of the type



(M = Ni(II), Cu(II); R = alkyl, aryl; the complexes are written simply as M–Sal–R). Ni–Sal–*n*-alkyl and Cu–Sal–*n*-alkyl, have a square-planar coordination structure,[2,3] the isomeric compounds Ni-(Cu)–Sal–*sec*-alkyl provided us with the first known examples of chelate compounds of nickel(II) and copper(II) that have a tetrahedral coordination structure.[4–8] The angle between the planes of the chelate rings, which indicates deviations from the regular tetrahedral structure, is 81° for Ni–Sal–isopropyl[8] and 60° for Cu–Sal–isopropyl.[9] It therefore appeared interesting to compare the magnetic properties of these complexes with those of the less distorted tetrahedral halo complexes of the same metals, and, for copper, with those of the square-planar isomers. The results are to be compared with the theoretical predictions of Figgis.[10,11]

(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) M. Stackelberg, *Z. anorg. allgem. Chem.*, **253**, 136 (1947); L. Sacconi, P. Paoletti, and G. Del Re, *J. Am. Chem. Soc.*, **79**, 4062 (1957); E. Frasson, C. Panattoni, and L. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959); E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Scheringer, and C. Freiburg, *Acta Cryst.*, **14**, 1222 (1961).

(3) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Inorg. Nucl. Chem.*, **19**, 73 (1961).

(4) L. Sacconi, P. L. Orioli, P. Paoletti, and M. Ciampolini, *Proc. Chem. Soc.*, 255 (1962).

(5) L. Sacconi and P. L. Orioli, *Ric. Sci. Rend.*, **32**, 645 (1962); S. Yamada and H. Nishikawa, *Bull. Chem. Soc. Japan*, **36**, 755 (1963).

(6) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963).

(7) L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, 276 (1964).

(8) M. R. Fox, E. C. Lingafelter, P. L. Orioli, and L. Sacconi, *Nature*, **197**, 1104 (1963); *Acta Cryst.*, **17**, 1159 (1964).

(9) P. L. Orioli and L. Sacconi, to be published.

(10) B. N. Figgis, *Nature*, **182**, 1568 (1958).

The variation of the magnetic susceptibilities of some Ni–Sal–aryl complexes, which are probably polymeric, has been measured from the temperature of boiling nitrogen to room temperature.

Experimental

Preparation of Compounds.—The complexes $(R_4N)_2MX_4$ (R = C_2H_5, n-C_3H_7; M = nickel(II), copper(II); X = Cl, Br, I) were prepared by the usual methods.[12] The Ni–Sal–R and Cu–Sal–R complexes were prepared by procedures already described.[6,7] The identity and purity of the compounds were checked by analysis of their nitrogen, halogen, and metal contents.

Magnetic Susceptibility Measurements.—The Gouy balance and the experimental technique have been described in a previous paper.[3] The reproducibility of our susceptibility values was about ±1%. No appreciable errors arose from temperature drifts during each measurement. Measurements on copper sulfate pentahydrate gave $\theta = 1°$K., $\chi_g^{292} = 5.97 \times 10^{-6}$ c.g.s. unit; literature values are $\theta = 1°$K., $\chi_g^{293} = 6.05 \times 10^{-6}$ c.g.s. unit.[13]

Results

At least fifteen measurements of the magnetic susceptibility between 80 and 300°K. were made on each case. The susceptibility follows a Curie–Weiss law, $\chi_A = \text{constant}/(T + \theta)$, within experimental error. Measured gram susceptibilities, χ_g, and molar susceptibilities fully corrected for diamagnetic contributions, χ_A, are given to only three temperatures in Table I. This table also lists the values of the Weiss constants θ and of the effective magnetic moments as calculated from $\mu_{\text{eff}} = 2.84\sqrt{\chi_A T}$.

Our values for the tetraalkylammonium salts of complexes MX_4^{2-} are in good agreement with those for other salts: $[(C_6H_5)_3CH_3As]_2NiCl_4$, $\mu_{\text{eff}}^{293} = 3.89$, $\theta = 35°$K.[12]; $[(C_2H_5)_4N]_2NiCl_4$, $\mu_{\text{eff}}^{293} = 3.87$ B.M.[12]; $[(C_2H_5)_4N]_4NiBr_4$, $\mu_{\text{eff}}^{293} = 3.79$ B.M.[12]; $[(C_6H_5)_3CH_3As]_2NiI$, $\mu_{\text{eff}}^{293} = 3.49$ B.M.[12]; $[(n\text{-}C_4H_9)_4N]_2NiI_4$, $\mu_{\text{eff}}^{300} = 3.47$ B.M., $\mu_{\text{eff}}^{74} = 3.25$ B.M.[14]; Cs_2CuCl_4, $\mu_{\text{eff}}^{293} = 2.00$ B.M.,[15] 1.96 B.M.,[12] $\theta = 1°$K.[15]; $[(C_2H_5)_4N]_2CuCl_4$, $\mu_{\text{eff}}^{293} = 1.97$ B.M.[16]; $[(C_6H_5)_3CH_3As]_2CuBr_4$, $\mu_{\text{eff}}^{293} = 1.96$ B.M.[12]

Discussion

Compounds of Nickel(II).—For tetrahedral complexes Figgis has shown that spin–orbit coupling should affect the pure crystal field levels in such a way that the Curie law breaks down and the magnetic moment increases with temperature: at 0°K., when the orbital contribution to the magnetic moment exactly cancels the spin contribution the moment becomes zero. At room temperature the moment for a regular tetrahedral nickel(II) complex is expected to be as high as 4.1 B.M. Recently Figgis, *et al.*,[11] have proved that the distortion of the tetrahedral structure as well as the delocalization of the unpaired electrons to the ligand orbitals reduces the size of the orbital contribution at all temperatures; thus the temperature dependence of the magnetic moment will be smaller. The values of μ_{eff} of $NiCl_4^{2-}$ and $NiBr_4^{2-}$ have been successfully interpreted on the basis of this conclusion.

At room temperature the orbital contribution to the magnetic moment of NiI_4^{2-} (Table I) is smaller and varies less with temperature than those of $NiCl_4^{2-}$ and $NiBr_4^{2-}$. It is likely that this differing behavior of NiI_4^{2-} is mainly due to a larger covalent character of the bonds rather than to a major distortion. Direct X-ray evidence is not available, but far-infrared data do not support the hypothesis of a large distortion of these compounds.[17] In fact the splitting of the infrared-active metal–halogen stretching vibrations gives some indication of the symmetry. Thus, the metal–halogen stretching mode is split in the compounds $[(C_2H_5)_4N]_2CuX_4$, which are quite likely largely distorted from the regular tetrahedral configuration,[18] but not in the compounds $[(C_2H_5)_4N]_2NiX_4$.[17]

Ni–Sal–isopropyl and Ni–Sal–*t*-butyl, on the contrary, have a largely distorted tetrahedral structure both because of the nonequivalence of the donor atoms and also because bond angles and bond lengths are not equal.[4,6,8] In view of these distortions, it is not surprising that these pseudo-tetrahedral complexes have an orbital contribution which is relatively small and only slightly temperature dependent. Actually, Ni–Sal–isopropyl and Ni–Sal–*t*-butyl have moments of 3.34 and 3.29 B.M., respectively, at room temperature: at 80°K. the moment of both complexes is 3.17 B.M. (Table I). These figures are in the range of μ_{eff} values for octahedral nickel(II) complexes, namely 3.1–3.3 B.M. It is of interest to note, however, that the magnetic moment of these pseudo-tetrahedral complexes decreases appreciably with temperature while those of octahedral complexes are virtually temperature independent[19] (see also the octahedral adduct Ni–Sal–*m*-chlorophenyl·2py, Table I).

In this connection, the magnetic behavior of some complexes Ni–Sal–aryl, paramagnetic in the solid state, is interesting. In fact, previous studies indicated that these complexes were not tetrahedral but more likely polymeric.[20] Their susceptibilities follow the Curie–Weiss law with $\mu_{\text{eff}}^{293} = 3.28$–$3.35$ B.M. and $-11°\text{K.} > \theta > -16°\text{K.}$ (Table I). These large values of θ show that the ground state of nickel(II) in these compounds is probably not as simple as in the mononuclear complexes.

Compounds of Copper(II).—The magnetic moment of a tetrahedral copper(II) complex is expected to decrease with temperature, having a value of *ca.* 2.2 B.M. at 193°K.[10] The magnetic moments of the tetra-

---

[11] B. N. Figgis, J. Lewis, F. Mabbs, and G. A. Webb, *Nature*, **203**, 1138 (1964).

[12] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

[13] B. N. Figgis and R. S. Nyholm, *ibid.*, 331 (1959).

[14] D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

[15] B. N. Figgis and C. M. Harris, *J. Chem. Soc.*, 855 (1959).

[16] C. Furlani and G. Morpurgo, *Theor. Chim. Acta*, **1**, 102 (1963).

[17] A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964).

[18] Large distortions are actually found in Cs_2CuCl_4 [L. Helmolz and R. F. Kruh, *ibid.*, **74**, 1176 (1952)], $[(CH_3)_4N]_2CuCl_4$ [B. Morosin and E. C. Lingafelter, *J. Phys. Chem.*, **65**, 50 (1961)], and Cs_2CuBr_4 [B. Morosin and E. C. Lingafelter, *Acta Cryst.*, **13**, 807 (1960)].

[19] R. Schlapp and W. G. Penney, *Phys. Rev.*, **42**, 666 (1932).

[20] L. Sacconi and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 1750 (1963).

TABLE I

MAGNETIC DATA FOR SOME NICKEL(II) AND COPPER(II) COMPLEXES AT VARIOUS TEMPERATURES

Compound	T, °K.	$\chi_g \times 10^6$	$\chi_A \times 10^7$	μ_{eff}, B.M.	θ, °K.
$[(C_2H_5)_4N]_2NiCl_4$	80	40.30	1880	3.48	+30
	156	23.40	1110	3.74	
	292	13.10	630	3.85	
$[(C_2H_5)_4N]_2NiBr_4$	79	30.30	1930	3.51	+18
	179	14.80	980	3.76	
	291	9.00	615	3.80	
$[(C_2H_5)_4N]_2NiI_4$	80	17.60	1700	3.31	+8
	192	7.40	745	3.40	
	291	4.80	505	3.44	
Ni–Sal–isopropyl	80	40.40	1570	3.18	+14
	200	17.50	690	3.33	
	291	11.90	475	3.34	
Ni–Sal–*t*-butyl	79	37.90	1580	3.17	+9
	194	15.90	675	3.25	
	293	10.90	470	3.29	
Ni–Sal–*m*-chlorophenyl	79	36.00	1900	3.48	−11
	173	14.60	785	3.31	
	294	8.20	455	3.28	
Ni–Sal-*p*-chlorophenyl	79	39.60	2080	3.64	−16
	195	13.60	735	3.40	
	292	8.60	470	3.33	
Ni–Sal–*m*-tolyl	79	42.80	2080	3.64	−14
	198	14.60	725	3.40	
	292	9.40	475	3.35	
Ni–Sal–*m*-chlorophenyl·2py	79	21.40	1490	3.08	+3
	195	8.40	605	3.09	
	294	5.40	405	3.10	
$[(C_2H_5)_4N]_2CuCl_4$	80	12.60	620	2.00	0
	180	5.20	273	1.99	
	294	2.95	169	2.00	
$[(C_2H_5)_4N]_2CuBr_4$	80	8.40	580	1.93	−2
	157	3.90	287	1.91	
	297	1.85	155	1.92	
Cu–Sal–*n*-propyl	79	13.50	545	1.86	+1
	176	5.80	244	1.85	
	291	3.25	147	1.86	
Cu–Sal–isopropyl	79	14.20	570	1.90	+2
	180	5.90	250	1.90	
	290	3.45	155	1.91	
Cu–Sal–*n*-butyl	79	12.40	515	1.85	0
	170	5.45	226	1.85	
	293	2.90	145	1.85	
Cu–Sal–*t*-butyl	79	13.40	580	1.92	+3
	159	6.35	280	1.92	
	291	3.25	158	1.93	

chlorocuprate and tetrabromocuprate ion are 1.93–2.00 B.M. and do not vary appreciably with temperature (Table I). It is clear that the orbital contribution is about half the expected value. Neither of these facts is very surprising since it is known that the coordination polyhedron is rather distorted in both anions.[18]

A comparison of the compounds of the type Cu–Sal–*n*-alkyl, which have the planar structure,[3] with those of Cu–Sal–isopropyl and Cu–Sal–*t*-butyl, which have a distorted tetrahedral structure,[5,7] is interesting. The susceptibilities of all compounds closely follow the Curie law (3°K. > θ > 0°K.), but the moments of the tetrahedral compounds are consistently slightly larger than those of planar isomers by *ca.* 0.05 B.M. (see Table I and ref. 7). This shows that the orbital contribution in a distorted tetrahedral case is slightly higher than in the planar case. The temperature dependence of the magnetic moment is negligible in both cases.

Finally $[(C_2H_5)_4N]_2CuBr_4$ and to a lesser extent $[(C_2H_5)_4N]_2CuCl_4$ show appreciably deviations from the Curie law near room temperature. This could be attributed to a small temperature-independent paramagnetism which is also present in other copper(II) compounds[21] though not in Cs_2CuCl_4,[15] but the reason for its absence in many other compounds of copper(II) is not clear.[15]

---

(21) R. S. Nyholm, *J. Chem. Soc.*, 1767 (1951).