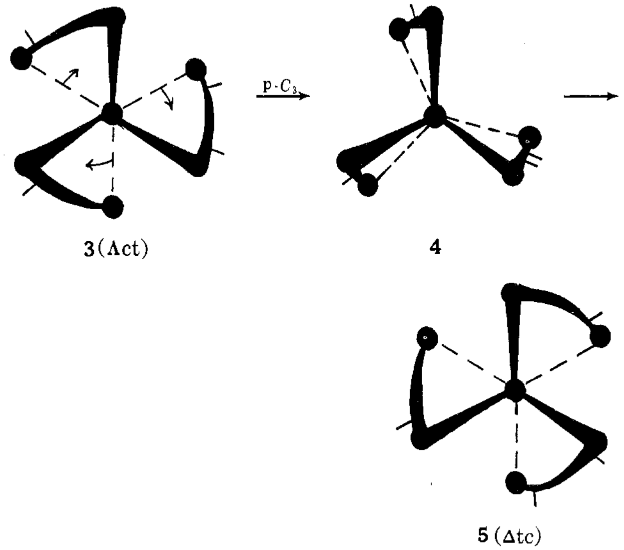


3(Λct) 4 5 (Δtc)

the diethyl complex and the two methyl signals of the Me,Ph complex observed above *ca.* −16 and −10°, respectively (*cf.* Figures 1 and 2). Kinetic parameters for bond rotation in Fe(Et$_2$dtc)$_2$mnt are given in Table I. $\Delta F^{\ddagger}$ values are identical within experimental error.

Because substitution of tfd by mnt increases the triplet state population the kinetic parameters for inversion of Fe(Et$_2$dtc)$_2$(S$_2$C$_2$R$_2$) can be examined in terms of N_t. The rate constant, *k*, and $\Delta F^{\ddagger}$, determined in the temperature region of exchange broadening, are the more accurate parameters from a total line shape analysis.[16] At −50° the rate of the mnt complex is faster than that of its tfd analog.[31] This rather small rate increase cannot, however, be interpreted in terms of experimentally different values of activation enthalpy or entropy changes. Interpretation of this effect will require additional measurements of inversion rates of other analogous tfd–mnt complexes and, possibly, a structural determination of an mnt complex if the conjecture that ground-state structures are related to the occurrence and rate of a p-C_3 twist is accepted.

Acknowledgments.—This research was supported in part by the Research Corporation and the University of Minnesota Graduate School and in part by the National Science Foundation under Grants GP-7576X and GP-18978X at M.I.T.

[31] N_t values for the two complexes at this temperature are estimated as 0.75 (mnt) and 0.12 (tfd[4]).

Contribution from the Department of Chemistry,
York University, Downsview, Ontario, Canada

Antiferromagnetic Exchange Interactions and Delocalization in Some Tetrahedral Binuclear Cobalt(II) Complexes of Phthalazine and Pyrazine Ligands

By A. B. P. LEVER,* L. K. THOMPSON, and W. M. REIFF

Received May 10, 1971

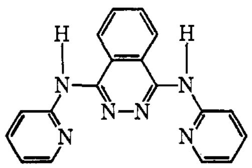
Some new cobalt complexes of the ligand 1,4-di(2′-pyridyl)aminophthalazine are reported and characterized by vibrational and electronic spectroscopy and magnetism. The complexes contain tetrahedrally coordinated cobalt(II) and are binuclear. The magnetic behavior (from 78 to 375°K) of species of this type are reported for the first time and demonstrate the presence of antiferromagnetically coupled ions. Similar data are reported for some previously reported binuclear tetrahedral cobalt(II) complexes of methylpyrazine and 2,5-dimethylpyrazine. The data were fitted to the standard equation for two spin-coupled $S = {}^3/_2$ ions using *J*, the exchange integral, and k^2, the delocalization coefficient, as variables. By allowing the temperature-independent paramagnetism to vary and using, for this term, a value of 10*Dq* derived from the electronic spectrum, excellent agreement between theory and experiment, as illustrated by a least-squares analysis, was obtained. All the complexes exhibited very weak exchange with *J* of the order of −1 to −5 cm^{-1}. Trends in k^2 which varied from about 0.5 to 1.05 were discussed in the light of current theory. The variations in *J*, k^2, and *B*, the Racah parameter, were rationalized in terms of the electronegativity of the coordinating halogens.

While binuclear complexes of divalent copper in which the metal atoms are fairly close together have been extensively investigated[1] and very large numbers of such complexes are known, relatively few such binuclear divalent nickel or cobalt complexes have been characterized. Some dimeric cobalt complexes of methylpyrazines[2] represented the first examples of binuclear cobalt complexes of tetrahedral stereochemistry in which exchange coupling might be expected to occur. Since then some syntheses of other binuclear cobalt species have been reported[3–9] but without detailed magnetic data. Recently attempts have been made to design ligands which have a strong tendency to coordinate to two metal atoms simultaneously and to constrain these two metal atoms to be in close proximity. Such ligands are generally quadridentate amines in which the two central nitrogen atoms are adjacent and are based in concept upon 2-pyridinealdazine, the first ligand shown to have such a capability.[10] Quite a few ligands of this general type

[1] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).
[2] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1235 (1962).
[3] K. Issleib and H. Weichmann, *Z. Anorg. Allg. Chem.*, **362**, 33 (1968).
[4] E. Wenschuh and B. Fritzsche, *ibid.*, **365**, 63 (1969).
[5] Y. Nakamura and S. Kawaguchi, *Chem. Commun.*, 716 (1968).
[6] E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, **4**, 391 (1969).
[7] J. L. Love and H. K. J. Powell, *Inorg. Nucl. Chem. Lett.*, **3**, 113 (1967).
[8] P. Bamfield, *J. Chem. Soc. A*, 81 (1968).
[9] S. V. Avakyan and R. A. Karapetyan, *Zh. Obshch. Khim.*, **35**, 1680 (1965).
[10] W. J. Stratton and D. H. Busch, *J. Amer. Chem. Soc.*, **80**, 1286, 3191 (1958); **82**, 4834 (1960).

have been reported.[11–19]

Derivatives containing a phthalazine ring seem particularly adept at forming binuclear complexes of this type. Blake, *et al.*,[14–16] have discussed the magnetic exchange characteristics of binuclear octahedral cobalt(II) and nickel(II) complexes of phthalazine ligands while we have published data for a series of binuclear copper complexes of a phthalazine ligand, namely, 1,4-di(2′-pyridyl)aminophthalazine (LH) (I).[19] The tetrahedral cobalt complexes of this ligand are now presented. In addition the exchange characteristics of some of the previously reported pyrazine cobalt dimers[2] are reported.



I

Experimental Section

Magnetic susceptibility measurements were obtained over the temperature range 78–370°K using the Faraday method with a fully automated apparatus[20] based on the Alpha 4-in. pole-piece variable-temperature magnetic balance. Mercury tetrathiocyanatocobaltate (II) was used as calibrant. Infrared spectra were obtained using Beckman Models IR-7 and IR-11 and electronic spectra with a Cary 14.

Cobalt was determined gravimetrically as $Co(py)_4(NCS)_2$. Prior to each analysis the sample was treated with a dilute solution of sodium dichromate in 0.1 *N* sulfuric acid to facilitate removal of the ligand as the insoluble dichromate salt.[19] C, H, and N analyses were carried out by Chemalytics Laboratories, Tempe, Ariz. Halogen analyses were carried out by a potentiometric method in aqueous solution using silver nitrate. LH is 1,4-di(2′-pyridyl)aminophthalazine.

Co_2LCl_3.—Cobalt chloride hexahydrate (3.3 g) was dissolved in methanol (100 ml) and the solution filtered. The ligand LH (2.0 g) was added and the mixture refluxed for 30 min. The solution (green when hot and red when cold) was filtered and its volume reduced until on warming a green crystalline product was obtained from the hot solution. The mixture was allowed to cool, the product filtered off, and the process repeated to obtain more product. The product was washed with a 1:1 methanol-ether mixture and recrystallized from methanol to give bright green crystals. The product was finely ground in a mortar in a drybag and dried under vacuum at 100° for 72 hr (yield 2.8 g (81%)). *Anal.* Calcd for $C_{18}H_{13}Cl_3Co_2N_6$: C, 40.2; H, 2.4; Cl, 19.8; Co, 21.9; N, 15.6. Found: C, 39.95; H, 2.6; Cl, 19.0; Co, 21.6; N, 15.8.

Co_2LBr_3.—Cobalt bromide hexahydrate (4.2 g) was dissolved in acetonitrile (120 ml) and the solution filtered. Owing to its limited solubility in acetonitrile the ligand LH (2.0 g) was soxhlet extracted into the metal salt solution. After a short time the product began to separate out as a green solid. When all the ligand had been extracted, the mixture was allowed to cool and the product was filtered off, washed with acetonitrile and ether, and dried. Purification was effected by soxhlet extraction in acetonitrile. The green product was dried under vacuum at 100° for 72 hr (yield 3.0 g (70%)). *Anal.* Calcd for $C_{18}H_{13}Br_3CoN_6$: C, 32.2; H, 1.95; Br, 35.7; Co, 17.6; N, 12.5. Found: C, 32.0; H, 2.2; Br, 35.8; Co, 17.0; N, 12.8.

The thiocyanate and iodide complexes $Co_2LH(NCS)_2(OH)_2$ and Co_2LI_3 were prepared in a similar fashion. With the exception of the cobalt thiocyanate complex all these complexes appear to be slightly moisture sensitive and were stored in a desiccator. *Anal.* Calcd for $C_{20}H_{15}Co_2N_8O_2S_2$ [$Co_2LH(NCS)_2(OH)_2$]: C, 41.3; H, 2.6; NCS, 19.9; N, 19.3. Found: C, 41.6; H, 3.0; NCS, 19.4; N, 19.4. *Anal.* Calcd for $C_{18}H_{13}Co_2I_3N_6$ (Co_2LI_3): C, 26.6; H, 1.6; N, 10.35. Found: C, 26.9; H, 3.0; I, 10.0. The pyrazine complexes were prepared as previously described.[2]

Computer Program.—Expression 4 for the exchange was initially solved by assuming $k = 1$ and iterating g and J to provide a solution with a minimum standard deviation from the experimental input data. A value of k was then derived from g *via* expression 5 and the original data recorrected for the TIP term with the new k value. A repeat iteration generated a new value of g and hence of k. The cycle was repeated until convergence occurred (usually four or five cycles were necessary). An IBM 360/50 was employed with the program written in A Programming Language (APL).

Results and Discussion

The Complexed Ligand.—The ligand L reacts with cobalt salts to yield the derivatives Co_2LX_3 (X = Cl, Br, I) and $Co_2LH(NCS)_2(OH)_2$. The green cobalt halide complexes are very soluble in water forming intense red-brown solutions from which buff-orange solids can be obtained. These buff solids have not yet been investigated. The cobalt complexes have little solubility in most organic solvents with the exception of methanol, in which solvolysis occurs (as in the case of water) with the formation of deep red-brown solutions.

The ligand L can be regarded as a 2-substituted pyridine derivative.[19] The A_{1g} symmetry ring breathing modes in benzene[21] and pyridine (A_1) which occur near 990 cm^{-1} in the infrared spectrum are also observed in 2-substituted pyridines and can be used as a reliable guide to the coordination of the pyridine residues.[22–27] This band is in general shifted to higher energies by 20–30 cm^{-1} on coordination. The ligand L exhibits a band in the infrared at 989 cm^{-1} which has been assigned to the ring breathing mode in the pyridine residues.[18,19] The 989-cm^{-1} band is absent in the complexes and an additional medium-intensity band occurs at 1009 cm^{-1} in the halides and 1019 cm^{-1} in the thiocyanate complex. Thus in all cases both pyridine residues of the ligand are coordinated to the metal ions.

The general similarity between the infrared spectra of the cobalt derivatives described here and the spectrum of the copper derivative $Cu_2LCl_3(OH)H_2O$, for which an X-ray structural study has been completed,[19,28] suggests that in all these complexes the ligand is quadridentate, coordinating through the two phthalazine nitrogens and the two pyridine nitrogens (see Figure 2 of ref 19).

The cobalt thiocyanate complex exhibits a band at 2086 cm^{-1} assigned to a C–N stretch in an isothiocyanate group[29] and a band at 482 cm^{-1} attributable

---

[11] W. J. Stratton, M. F. Rettig, and R. F. Drury, *Inorg. Chim. Acta*, **3**, 97 (1969).

[12] W. J. Stratton, *Inorg. Chem.*, **9**, 517 (1970).

[13] W. J. Stratton and P. J. Ogren, *ibid.*, **9**, 2588 (1970).

[14] J. E. Andrew, P. W. Ball, and A. B. Blake, *Chem. Commun.*, 143 (1969).

[15] J. E. Andrew and A. B. Blake, *J. Chem. Soc. A*, 1408 (1969).

[16] P. W. Ball and A. B. Blake, *ibid.*, *A*, 1415 (1969).

[17] R. Robson, *Aust. J. Chem.*, **23**, 2217 (1970).

[18] N. H. Pilkington and R. Robson, *ibid.*, **23**, 2225 (1970).

[19] L. K. Thompson, V. T. Chacko, J. A. Elvidge, A. B. P. Lever, and R. V. Parish, *Can. J. Chem.*, **47**, 4141 (1969).

[20] J. C. Donini, B. Hollebone and A. B. P. Lever, submitted for publication.

[21] C. H. Kline and J. Turkevitch, *J. Chem. Phys.*, **12**, 300 (1944).

[22] A. R. Katritzky and A. R. Hands, *J. Chem. Soc.*, 2202 (1958).

[23] D. A. Baldwin, A. B. P. Lever, and R. V. Parish, *Inorg. Chem.*, **8**, 107 (1969).

[24] S. P. Sinha, *Spectrochim. Acta*, **20**, 879 (1964).

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

[26] R. A. Russell and H. W. Thompson, *J. Chem. Soc.*, 483 (1955).

[27] M. Keeton and A. B. P. Lever, *Inorg. Chem.*, **10**, 47 (1971).

[28] E. C. Lingafelter and G. Marongiu, to be submitted for publication.

[29] J. L. Burmeister, *Coord. Chem. Rev.*, **1**, 205 (1966).

TABLE I

ELECTRONIC SPECTRA (MULL TRANSMITTANCE)

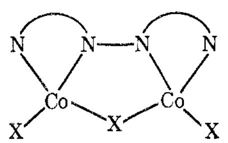
	λ_{max}, cm^{-1} (shoulders in parentheses)								
Compound	$^4T_1(F) \rightarrow {}^4A_2$				$^4T_1(P) \leftarrow {}^4A_2$				$\pi-\pi^*$
Co_2LCl_3	5500	6200	8350	10,500	14,500	15,000	18,000	18,900	28,600
Co_2LBr_3		5650	7900	10,600	13,900	14,300	15,000 (15,600) 16,700	18,400	28,200
Co_2LI_3		5200	7300	10,300	13,000	13,900	14,500 15,600	17,500	27,800
$Co_2LH(NCS)_2(OH)_2$			(7000)	8,000			16,000 (17,000)		29,400

to an N–C–S bend in such an isothiocyanate group. The corresponding C–S stretching mode[29] could not be found in the region 780–860 cm^{-1}. It is probably hidden among the absorptions associated with the ligand itself in this region.

In the far-infrared region bands have been tentatively assigned to terminal and bridging cobalt–chlorine stretching vibrations in the complex Co_2LCl_3 at 330 and 155 cm^{-1}, respectively.[30] The ligand itself does not absorb in these regions. By comparison a strong band at 263 cm^{-1} in the spectrum of the bromide complex Co_2LBr_3 has been assigned to terminal cobalt–bromine stretch. A strong broad band observed in the spectrum of the iodide complex Co_2LI_3 at 190 cm^{-1} may be associated with terminal cobalt–iodine stretch. The poor definition of the spectra in this region prevented any further positive assignments. On the basis of the similarity between the spectra of the halide complexes in the range 4000–650 cm^{-1} the bromide and iodide complexes are also expected to have bridging halogen groups.

The complexes exhibit bands in their mull transmittance spectra at room temperature (Table I) typical[31] of pseudotetrahedral cobalt(II). In the near-ultraviolet region the halide complexes exhibit fairly intense absorptions between 28,600 and 27,800 cm^{-1} which are assigned to $\pi-\pi^*$ transitions in a monoanionic ligand (Table I). It had earlier been demonstrated with a series of copper(II) complexes with this ligand[14] that the lowest energy ultraviolet absorption due to the ligand fell into two well-defined ranges depending upon whether the ligand was neutral or anionic, with the former lying at higher energy. The division into two ranges does not appear to be clear-cut in the case of the cobalt complexes. The thiocyanate is formulated to contain neutral ligand because of the higher energy of the ultraviolet band. However the evidence is ambiguous and its formulation as $Co_2L(NCS)_2(OH)(H_2O)$ containing anionic ligand cannot be excluded. The two formulations may in fact be closely related if the hydrogen atom concerned is hydrogen bonded between an OH group and a ligand nitrogen atom. The distinction then becomes almost semantic.

The evidence presented above for the cobalt complexes, together with their relationship to the copper complexes previously described[19] and for which X-ray data are available,[19,28] leaves little doubt that these complexes are correctly formulated as tetrahedral binuclear cobalt(II) derivatives with the basic structural unit shown (II). In the case of the thiocyanate complex, the hydroxy group is assumed to be bridging since the infrared spectrum excludes the presence of bridging thiocyanate groups.



II

Magnetic Properties.—The magnetic data for the complexes of this investigation are found in Table II. All of the cobalt complexes exhibit temperature dependence of their magnetic moments over the temperature range 370–80°K. Regular tetrahedral cobalt(II) complexes have moments[32] typically in the range 4.4–4.8 BM. Pseudotetrahedral cobalt complexes of the type CoL_2X_2 where X is Cl, Br, I, etc. and L is one of a variety of monodentate ligands (benzimidazole, Ph_3P, Ph_3PO, Ph_3As, Ph_3AsO) also have magnetic moments which cluster in the range 4.5–4.8 BM with little or no temperature dependence.[33,34] For this reason such complexes are generally treated as though they were tetrahedral, an assumption which will be made here.

It is significant that the moments of three of the cobalt systems go below the spin-only value and in the case of iodide complex by nearly 0.3 BM. The data suggest rather weak antiferromagnetic exchange between the metal atoms (intramolecular) and provide supporting evidence of the polynuclear nature of these systems.

Variable-temperature magnetic data for such interacting tetrahedral cobalt(II) ions have not been previously reported. The isolated cobalt(II) ion in a tetrahedral environment has a spin of $^3/_2$ and is orbitally nondegenerate ($^4A_2$ ground term). Exchange coupling of two such ions leads to spin states of $S = 0, 1, 2,$ and 3, with the diamagnetic state lying lowest if the exchange is antiferromagnetic in nature (J negative). This is evidently so in this series. The molar susceptibility for such a system is given by[35]

$$x = \frac{N\beta^2 g^2}{3kT}\left[\frac{42 + 15e^{6x} + 3e^{10x}}{7 + 5e^{6x} + 3e^{10x} + e^{12x}}\right] \qquad (1)$$

where $x = -J/kT$ and the other terms have their usual significance. This equation is derived by using the Van Vleck equation[36] and assuming the presence of the four spin states lying at 0, $2|J|$, $6|J|$, and $12|J|$

---

(30) C. Postmus, J. R. Ferraro, A. Quattrochi, K. Shobatake, and K. Nakamoto, *Inorg. Chem.*, **8**, 1851 (1969).

(31) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1968.

(32) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 12 (1954).

(33) M. Goodgame and F. A. Cotton, *J. Amer. Chem. Soc.*, **84**, 1543 (1962).

(34) F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *ibid.*, **83**, 1780 (1961).

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

(36) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.

in energy. The orbital contribution is assumed to be zero. In such circumstances g, the Lande splitting factor, is equal to 2.00. However, although the ground state of the cobalt(II) ion in a tetrahedral environment is an orbital singlet ($M_L = 0$), an orbital contribution is mixed into this ground state both by spin–orbit coupling and by the magnetic field (second-order Zeeman effect).[37] As a consequence the g factor instead of being equal to 2.00 becomes

$$g = 2\left(1 - \frac{4\lambda_0}{10Dq}\right) \tag{2}$$

where λ_0, the spin–orbit coupling coefficient, is negative for cobalt(II) (-172 cm^{-1} for the free-ion term). The second-order Zeeman effect gives rise to the so-called temperature-independent paramagnetism, in this case $8N\beta^2/10Dq$. Both of these effects are larger than the exchange interaction J, which is only of the order of a few wave numbers and should therefore be unaffected by it. In deriving the above expressions for the spin–orbit coupling interaction and the second-order Zeeman effect, the assumption is made that the wave functions involve solely d orbitals. However tetrahedral complexes of the later transition metals are fairly covalent and the symmetry is such that mixing of the d orbitals with ligand orbitals by both a σ and a π mechanism is feasible, and the assumption that the basis set involves only d orbitals is erroneous. This has two consequences: (i) application of the orbital angular momentum operator L to the basis set will yield values which are incorrect since the set will include p orbitals as well as d orbitals; (ii) the value of the spin–orbit coupling coefficient will be modified. Rather than derive an accurate basis set which would be most difficult, two approximations are made. First, to take (i) into account, L is replaced by KL where K is called the "delocalization coefficient."[38,39] In a similar manner for (ii) λ_0 is replaced[40] by $R\lambda_0$. The parameter K^2 is a measure of the contribution of ligand (p orbital) wave functions to the total wave function of the ground state of the metal atom and is therefore related to the molecular orbital coefficients describing this mixing and to the metal–ligand overlap integral.[41–44] The various approaches to the calculation of K^2 have recently been discussed in depth.[38,41] If overlap is small (less than 0.5), which is certainly going to be the case here, then K^2 is less than unity and will approach 0.5 as the mixing coefficient approaches 0.5 (from eq 34 of ref 41). Values of K^2 above unity would not be anticipated when the metal–ligand overlap is small.[41]

The spin–orbit coupling coefficient is proportional to the fourth power of the nuclear charge experienced by the electrons concerned.[45] In complex molecules a deviation of this coefficient from the free-ion value may arise through two related phenomena. First, a covalent interaction with the ligand will place ligand charge between the nucleus and the electron thereby expanding the d-electron cloud decreasing the effective nuclear charge and decreasing both λ and B.[45,46] Second, if the covalent interaction is sufficiently great for the d electron to spend appreciable time on the ligand, then it will be influenced by the nuclear attraction of the ligand. If the ligand is a heavy atom, then its Z^4 contribution may be more important than the contribution from the metal itself, thereby raising the value of λ above the metal free-ion value. The coefficient R allows for these two related effects and may clearly be less than or greater than unity. In this fashion expression 2 becomes

$$g = 2\left(1 - \frac{4KR\lambda}{10Dq}\right) \tag{3}$$

and the temperature-independent paramagnetism (TIP) becomes $8N\beta^2K^2/10Dq$. By combining these equations it is evident that the magnetic susceptibility of the complexes in question should be describable in terms of three unknowns, namely, J, R, and K ($10Dq$ being obtained from the electronic spectrum). However the data are not sensitive toward R and K as independent parameters. Instead therefore the assumption[37] is made that $R = K$, and hence the susceptibility will be given by

$$\chi_{\text{total}} = \chi(\text{exchange, eq 1}) + 8N\beta^2K^2/10Dq \tag{4}$$

where g is now

$$g = 2\left(1 - \frac{4K^2\lambda_0}{10Dq}\right) \tag{5}$$

The experimental data (Table II) can be fitted to within experimental error with the two variables K and J, which are the only unknowns in eq 4. For the reason indicated[39] the data are presented (Table III) in terms of k and J and the variations of K and R inferred therefrom (*vide infra*). The perfect agreement between experiment and theory does not, of course, justify the accuracy of the basic model or the assumptions, such as $R = K$, inherent therein and electron spin resonance data would constitute useful additional corroborative information. Data for the dimeric pyrazine cobalt halides are also included in Tables II and III.

The exchange interaction is extremely small, particularly so in the case of the pyrazine derivatives.[47] The cobalt–cobalt distances in these derivatives are unknown but simple geometry assuming no excessive distortion of the molecule requires a distance of approximately 3.0–3.4 Å in both the phthalazine and pyrazine series. In the complex $Cu_2LCl_3(OH)H_2O$ the Cu–Cu distance[28] is 3.00 Å.

The exchange is halogen dependent in both series with $|J|$ increasing with decreasing electronegativity of the halogen (optical electronegativities fall in the

---

[37] B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966.

[38] M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, **10**, 1 (1968).

[39] There is confusion in the literature concerning this parameter since k^2 may be used to designate both the square of the delocalization coefficient and the product Rk, depending upon whether the author concerned decides to recognize the independent existence of R or not. To avoid confusion in this paper the capital letter K will be used for the delocalization constant. The product k^2 will be retained and defined as $k^2 = fKR$ where f is approximately unity, but not exactly unity, because of the way in which we have analyzed our data (see text).

[40] J. Owen and J. H. M. Thornley, *Rep. Progr. Phys.*, **29**, 676 (1966).

[41] J. J. Salzman and H. H. Schmidtke, *Inorg. Chim. Acta*, **3**, 207 (1969), and references therein.

[42] A. A. Misetich and R. E. Watson, *Phys. Rev.*, **143**, 335 (1966).

[43] B. R. McGarvey, *Transition Metal Chem.*, **3**, 90 (1966).

[44] B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

[45] C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, 1962.

[46] W. Marshall and R. Stuart, *Phys. Rev.*, **123**, 2048 (1961).

[47] J is derived on the basis that $R = K$. The error in J arising from the fact that this assumption is not strictly valid will be very small.

TABLE II

MAGNETIC DATA[g]

Temp, °K	$10^6\chi'_m$,[b] cgsu	μ,[c] BM	Temp, °K	$10^6\chi'_m$,[b] cgsu	μ,[c] BM
Co_2LCl_3 (113×10^{-6})[a]			Co_2LBr_3 (134×10^{-6})		
81.6	24,770	4.02	80.6	22,785	3.83
109.9	19,570	4.15	99.2	19,280	3.91
130.5	16,545	4.16	133.9	14,850	3.99
147.4	14,810	4.18	151.2	13,310	4.01
201.2	11,215	4.25	169.7	12,040	4.04
219.1	10,580	4.31	187.9	11,060	4.08
237.1	9,820	4.32	206.1	10,150	4.09
256.0	9,140	4.33	224.5	9,420	4.11
274.8	8,570	4.34	242.4	8,740	4.11_5
293.7	8,060	4.35	272.0	7,970	4.15
312.8	7,620	4.37	299.6	7,250	4.17
331.0	7,230	4.38	318.6	6,870	4.18
349.4	6,880	4.39	337.3	6,540	4.20
367.8_5	6,570	4.40	356.3	6,240	4.22
370.7	6,540	4.40	375.1	5,970	4.23
$(2,5\text{-DMPZ})CoBr_2$[f] (138×10^{-6})			$(2\text{-MPZ})CoBr_2$[e] (126×10^{-6})		
83.0	29,170	4.40	81.3	29,220	4.36
100.7	24,450	4.44	85.6	28,590	4.43
118.1	21,030	4.46	103.1	24,000	4.45
135.4	18,420	4.47	120.5	20,705	4.47
152.9	16,420	4.48	138.0	18,180	4.48
171.0	14,790	4.50	156.2	16,270	4.51
190.4	13,375	4.51	174.6	14,660	4.52_5
207.9	12,320	4.53	191.9	13,400	4.54
226.6	11,530	4.57	210.8	12,310	4.56
245.5	10,690	4.58	229.9	11,330	4.57
264.5	9,980	4.60	248.4	10,510	4.57
283.2	9,370	4.61	267.6	9,820	4.59
302.1	8,800	4.61	285.9	9,250	4.60
321.1	8,320	4.62	305.1	8,720	4.61
339.7	7,900	4.63	323.6	8,250	4.62
358.9	7,530	4.65	342.1	7,860	4.64
371.8	7,310	4.66			
$Co_2LH(NCS)_2(OH)_2$ (132×10^{-6})			Co_2LI_3[d] (155×10^{-6})		
80.9	22,120	3.78	81.4	19,980	3.61
99.4	19,030	3.89	99.7	17,420	3.73
116.9	16,530	3.93	117.0	15,315	3.79
134.4	14,600	3.96	134.5	13,750	3.85
151.5	13,120	3.99	151.8	12,370	3.88
169.7	11,900	4.02	170.2	11,260	3.92
187.9	10,905	4.05	188.7	10,330	3.95
206.0	10,025	4.06_5	207.1	9,550	3.98
224.2	9,290	4.08	225.6	8,880	4.00
261.1	8,105	4.11_5	244.6	8,250	4.02
279.7	7,740	4.16	301.1	6,910	4.08
296.6	7,330	4.17	320.1	6,550	4.10
314.4	6,960	4.19	338.6	6,240	4.11
332.9	6,610	4.19_5	341.7	6,190	4.11_5
347.0	6,360	4.20			
$(2\text{-MPZ})CoI_2$[e] (158×10^{-6})					
82.7	28,435	4.34	211.6	12,020	4.51
86.2	27,340	4.34	231.0	11,120	4.53
104.6	22,965	4.38_5	249.1	10,340	4.54
121.9	19,940	4.41	267.7_5	9,695	4.56
139.7	17,395	4.41	286.6	9,090	4.57
157.3	15,650	4.44	305.9_5	8,580	4.58
175.3	14,300	4.48	324.6_5	8,135	4.60
193.3	13,055	4.49	344.5	7,710	4.61

[a] Diamagnetic correction given in parentheses. [b] χ'_m, corrected molar susceptibility. [c] μ, magnetic moment. [d] Magnetic data vary slightly from one sample to another; this is a mean set of data. [e] 2-MPZ is 2-methylpyrazine. [f] 2,5-DMPZ is 2,5-dimethylpyrazine. [g] The absolute accuracy of the magnetic data is not guaranteed to be better than 1% but within a set of data the relative accuracy should be 0.25%.

sequence Cl (3.0) > Br (2.8) > NCS (2.6) > I (2.5)).[45,48] It is evident that as the positive charge on the cobalt atom decreases, the d orbitals expand and the exchange is enhanced. The nephelauxetic interelectronic repulsion parameter *B* in the halogen series reflects this increased charge donation in that the lowest values of *B* are observed with the iodo complexes. The thiocyanate complex is anomalous as expected.[49] The above data do not discriminate between a direct exchange or a superexchange mechanism. There is some evidence, however, pointing to the latter. The iodo(methylpyrazine) complex has a higher value of *J* than the bromo(methylpyrazine) derivative, yet the former, unless there is gross distortion of the Co–I–Co angle, will have the longer Co–Co bond. In the related $S = {}^3/_2$ $Cr_2X_9{}^{3-}$ ions replacement of X = Cl by X = Br results in a longer bond and a smaller value of *J*,[50] and a correlation is observed between the exchange interaction, presumably direct in this case, and the Cr–Cr bond length. Since the reverse behavior is observed in the cobalt complexes, a superexchange mechanism may be involved.

TABLE III

SPECTROSCOPIC AND MAGNETIC PARAMETERS[a]

Complex	10*Dq*, cm^{-1} [b]	*B*, cm^{-1} [b]	k^2	*g*	*J*, cm^{-1}	SD, BM[c]
Co_2LCl_3	4990	568	0.86	2.24_7	-3.39_5	0.016
Co_2LBr_3	4790	576	0.60	2.17_8	-4.33	0.015
Co_2LI_3	4520	553	0.51	2.15_0	-5.49	0.025
$Co_2LH(NCS)_2(OH)_2$	4360	728	0.54_5	2.17_7	-4.45	0.022
$Co_2(2\text{-MPZ})_2Br_4$	4380	676	1.04	2.336	-1.56	0.012
$Co_2(2\text{-MPZ})_2I_4$	4160	617	0.97	2.32_9	-2.14	0.012
$Co_2(2,5\text{-DMPZ})_2Br_4$	4330	675	1.06	2.34_7	-2.24	0.016

[a] k^2, *g*, and *J* were obtained from a least-squares analysis of the data using eq 4. [b] Obtained from the electronic spectrum (see text). [c] Standard deviation of the magnetic moment (see Table II). The TIP corrections involved in each of the above complexes may be calculated from the data using TIP = $2.088k^2/10Dq$ cgsu.

Values of the parameter[39] k^2 are also included in Table III. The accuracy of their evaluation is dependent on the accuracy of 10*Dq* and on the viability of the model chosen. It is common practice[31] to average the energy of the multiple bands occurring in the near-infrared and in the visible regions of tetrahedral cobalt spectra and use these averages as the positions of the ${}^4T_1(F) \leftarrow {}^4A_2$ and ${}^4T_1(P) \leftarrow {}^4A_2$ transitions, respectively. This procedure was employed here but the band near 18,000 cm^{-1} was excluded since it is believed to be primarily quartet–doublet in nature.[31] In that the same procedure was employed for all the complexes, the errors, if present, in the evaluation in 10*Dq* should be systematic. The values for 10*Dq* in Table III are probably good to within 10% placing similar limits on k^2. Despite this uncertainty in k^2, these data exhibit some well-defined trends. In the phthalazine series k^2 depends upon X, decreasing in the sequence Cl > Br > NCS > I. Values for k^2 in the pyrazine series exceed those in the phthalazine series.

In discussing these data the initial assumption that $K = R$ can be discarded. A low value of k^2 (phthalazine series) (less than 0.7) implies that both *K* and *R* are less than unity, while the higher values of k^2 observed in the pyrazine series require that *R* exceed unity.

The low values in the phthalazine series may be reconciled if the ligand is regarded as a good electron

---

(48) H. H. Schmidtke, *Proc. Int. Conf. Coord. Chem.*, *1968*, **11** (1968).

(49) B. R. Hollebone, *J. Chem. Soc. A*, 481 (1971).

(50) I. E. Grey and P. W. Smith, *Aust. J. Chem.*, **24**, 73 (1971).

acceptor. The presence of the ring nitrogen atoms, the length of the conjugated pathway, and the fact that the ligand is attached at two sites to the metal would justify such a viewpoint. The amount of electron transfer would increase with decreasing effective nuclear charge on the metal as the group X becomes less electronegative. It is significant that k^2, J, and B, which are all quite independent parameters, exhibit parallel trends in this respect (the B value for the thiocyanate complex being an exception).[49] The pyrazine series differs in its microstoichiometry ($CoNX_3$ rather than CoN_2X_2) from the phthalazine series. This ligand is known to be a good electron acceptor[51] and can act as an electron sink to allow a greater cobalt–halogen covalent interaction. R exceeds unity in this series but not in the phthalazine series because of the greater number of heavy atoms surrounding the cobalt atom. It is significant that in the CoX_4^{2-} series R is less than unity[37] ($k^2 < 1$)[41] presumably because in the absence of a ligand such as pyrazine to act an an electron sink, the cobalt–halogen interaction is decreased.

The above discussion is speculative and further cobalt systems are under study to corroborate the approach. If K and R can be independently determined and their meaning clarified, they may prove to be most powerful probes into our understanding of transition metal chemistry.

Acknowledgments.—This work, carried out in part at York University and in part at the University of Texas, was supported by the Robert A. Welch Foundation, the U. S. Atomic Energy Commission, the National Science Foundation, and the National Research Council (Ottawa, Canada). We are also indebted to J. C. Donini for computer programming assistance, B. S. Ramaswamy for experimental assistance, and B. R. Hollebone for useful discussions.

---

[51] A. B. P. Lever, S. M. Nelson, and T. M. Shepherd, *Inorg. Chem.*, **4**, 810 (1965).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
OREGON STATE UNIVERSITY, CORVALLIS, OREGON 97331

Methanolysis of Tetrakis(phosphorus trichloride)nickel(0)[1]

BY DAVID F. BACHMAN, EDWIN D. STEVENS, THOMAS A. LANE, AND JOHN T. YOKE*

Received May 21, 1971

Methanolysis of $[Ni(PCl_3)_4]$ in hydrocarbon solvents is a slow heterogeneous oxidation–reduction process. Products typical of the methanolysis of uncoordinated phosphorus trichloride are formed; these include methyl chloride and dimethyl hydrogen phosphonate. The oxidation product is $[Ni(CH_3OH)_6]^{2+}$. No hydrogen is formed, and the initial reduction product is methyl hypophosphite which decomposes to phosphine and other products. A hydridonickel intermediate is suggested by a transient ir absorption at 1610 cm^{-1} (shifted to 1135 cm^{-1} on deuteration), but no high-field nmr signal could be observed. When methoxide ion is made the nucleophile, the simple reaction product $[Ni(P(OCH_3)_3)_4]$ is obtained in high yield. Treatment of this with hydrogen chloride leads to slow hydrogen formation.

Introduction

Alcoholysis of phosphorus trichloride[2] results in an Arbuzov-type rearrangement, involving the lone pair of electrons and a change in the coordination number of phosphorus

$$:PCl_3 + 3ROH \longrightarrow HP(O)(OR)_2 + 2HCl + RCl$$

The tertiary ester $:P(OR)_3$ is commonly prepared by having a tertiary amine present to bind hydrogen chloride or may be obtained using sodium alkoxide in an inert medium

$$:PCl_3 + 3NaOR \longrightarrow :P(OR)_3 + 3NaCl$$

In tetrakis(phosphorus trichloride)nickel(0), $[Ni(PCl_3)_4]$, the coordination number of phosphorus is already four and the lone pair is involved in the coordinate bond. Smith[3] reported that this compound "dissolves in alcohols but decomposition with the formation of green solutions is quite rapid."

A century ago,[4] the methanolysis of phosphorus trichloride coordinated to platinum(II) and palladium(II) chlorides was reported to give the corresponding complexes of trimethyl phosphite. Similar synthesis of the trimethyl phosphite complex has been reported with gold(I)[5] and copper(I).[6] Since an Arbuzov rearrangement about phosphorus did not occur in those cases, retention of the metal–phosphorus bond during the reaction is implied.

We have studied the reaction of $[Ni(PCl_3)_4]$ with methanol and with methoxide ion in hydrocarbon solvents in some detail. Kruck and Höfler have reported[7] the preparation of tetrakis(trimethyl phosphite)nickel(0) by the reaction of sodium methoxide with the analogous phosphorus trifluoride complex.

Experimental Section

Materials.—Tetrakis(phosphorus trichloride)nickel(0)[3] was recrystallized from pentane or hexane immediately prior to use. Matheson nickel carbonyl and hydrogen chloride were used

---

[1] Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970; see Abstract No. INOR 97.

[2] G. M. Kosolapoff, "Organophosphorus Compounds," Wiley, New York, N. Y., 1950, Chapter 8; J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience, New York, N. Y., 1958, pp 372–373.

[3] W. C. Smith, *Inorg. Syn.*, **6**, 201 (1960).

[4] P. Schutzenberger, *C. R. Acad. Sci.*, **70**, 1414 (1870); *Bull. Soc. Chim. Fr.*, **14**, 178 (1870); **18**, 101 (1872).

[5] M. Levi-Malvano, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, **17**, 847 (1909).

[6] T. L. Davis and P. Ehrlich, *J. Amer. Chem. Soc.*, **58**, 2151 (1936).

[7] T. Kruck and M. Höfler, *Angew. Chem.*, **79**, 582 (1967).