CN^- systems; like Ni^{2+}, Zn^{2+} shows nonstepwise complex formation ($Zn(CN)_2(aq)$), while, like Hg^{2+}, stepwise complex ion formation is also observed ($Zn(CN)_3^-$, $Zn(CN)_4^{2-}$).

The trends in the $\Delta G°$, $\Delta H°$, and $T\Delta S°$ values as a function of i for the Ni^{2+}–CN and Zn^{2+}–CN^- systems are shown in Table II. The values in Table II were obtained by dividing the total quantity in each case by i, *e.g.*, $\Delta H_4°$ for each system ($M^{2+} + 4CN^- = M(CN)_4^{2-}$) was divided by 4.

TABLE II

$\Delta G°/i$, $\Delta H°/i$, and $T\Delta S°/i$ VALUES (KCAL./MOLE) CALCULATED FOR THE REACTION $M^{2+} + iCN^- = M(CN)_i^{2-i}$

i	$\Delta G°/i$	$\Delta H°/i$	$-T\Delta S°/i$
		M = Zn	
2	−7.55	−5.4	−2.2
3	−7.30	−6.4	−0.9
4	−6.69	−7.0	0.3
		M = Ni	
4	−10.3	−10.8	0.5

Since $\Delta G° = \Delta H° - T\Delta S°$, it is interesting that the $\Delta H°/i$ and $-T\Delta S°/i$ values diverge with increasing i in the Zn^{2+}–CN^- system and, since the change of $-T\Delta S_i°$ with i is greater than is that of $\Delta H_i°$, $\Delta G_i°$ values become more positive with increasing i, resulting in stepwise formation of $Zn(CN)_3^-$ and $Zn(CN)_4^{2-}$. Our understanding of nonstepwise complex formation where it occurs in these M^{2+}–CN^- systems is severely hampered by the fact that no data are available in aqueous solution for the formation of the obviously less stable intermediate complexes. Statistically, it is hardly conceivable that these intermediate species do not form; however, if they do, it must be in heretofore undetectable concentrations. Thus, one can only estimate the thermodynamic properties of these species. The absence of the $ZnCN^+$ species, for example, must be explained by the $\Delta G_1°$ value being sufficiently more positive than the $\Delta G_2°$ value to cause the $Zn(CN)_2(aq)$ species to predominate in the $\bar{n}$ region 0 to 2. No data indicating Ni^{2+}–CN^- complexes lower than $Ni(CN)_4^{2-}$ have been reported, and available equilibrium constant values[22] for the formation of the $Ni(CN)_5^{3-}$ and $Ni(CN)_6^{4-}$ species show that $\Delta G_4°$[4] is more negative than $\Delta G_5°$ or $\Delta G_6°$ by approximately 41 kcal./mole. Thus, the $Ni(CN)_4^{2-}$ species shows maximum stability in this system. As seen in Table II, the magnitude of $\Delta G_4°$ in the Ni^{2+}–CN^- system is determined by that of $\Delta H_4°$; the $T\Delta S_4°$ term being small and of the same order of magnitude as that for the corresponding Zn^{2+} complex. The larger $\Delta H_4°$ value of Ni^{2+} compared to that of Zn^{2+} is undoubtedly a result of the ligand field stabilization of the $Ni(CN)_4^{2-}$ species by CN^-. Such stabilization does not occur with the d^{10} metal ion Zn^{2+}, and this fact parallels the marked $\Delta H_4°$ difference in the formation of their respective tetracyano complex ions.

Acknowledgments.—The authors wish to express appreciation to Mrs. Arlene Hill and Mr. Nolan Edmunds for performing the thermometric titration determinations, and to Mrs. Judie Eatough for several helpful discussions.

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[22] R. A. Penneman, R. Bain, G. Gilbert, L. H. Jones, R. S. Nyholm, and G. K. N. Reddy, *J. Chem. Soc.*, 2266 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Studies of Nitro and Nitrito Complexes. II. Complexes Containing Chelating NO_2 Groups

BY D. M. L. GOODGAME AND M. A. HITCHMAN

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The preparations of $CoL_2(NO_2)_2$ (L = $(C_6H_5)_3PO$, $(C_6H_5)_3AsO$), $Ni\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}(NO_2)_2$, and $NiL_2(NO_2)_2$ (L = quinoline, α-picoline) are described. The first three compounds are monomeric in acetone or chloroform. The magnetic moments at room temperature and the electronic and infrared spectra of the complexes are reported. The results of the physical measurements suggest that the anions in these compounds are coordinated as bidentate, chelating groups.

Introduction

The nitrite ion is known to coordinate to metal ions in a variety of ways. As a monodentate ligand it may bond either through nitrogen, forming the well-known nitro complexes, or through one of the oxygen atoms to give the less-common nitrito complexes. It may also function as a bridging group, as in $\{(n\text{-}C_4H_9)_3P\}_2Pd_2(NO_2)_4$,[1] with nitrogen and one of the oxygen atoms acting as the donor atoms.[1,2] During studies carried out to investigate the factors influencing the mode of coordination of the nitrite ion we recently prepared

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(1) J. Chatt, L. A. Duncanson, B. M. Gatehouse, J. Lewis, R. S. Nyholm, M. L. Tobe, P. F. Todd, and L. M. Venanzi, *J. Chem. Soc.*, 4073 (1959).

(2) K. Nakamoto, J. Fujita, and H. Murata, *J. Am. Chem. Soc.*, **80**, 4817 (1958).

a series of complexes of the type $ML_2(NO_2)_2$ (where M = Co(II) or Ni(II) and L is an uncharged ligand) in which the anions appear to be bonded in a way hitherto unrecognized for NO_2^-, namely as bidentate, *chelating* groups. We report here the preparation and properties of these compounds.

Experimental

Preparation of Compounds. **$Co\{(C_6H_5)_3PO\}_2(NO_2)_2$.**—A solution of $Co\{(C_6H_5)_3PO\}_2Cl_2$ in dry acetone was shaken with a twofold excess of finely powdered silver nitrite. The resulting mauve solution was filtered and then evaporated *in vacuo* until mauve crystals formed, together with a small amount of a brown solid. The solid products were filtered off, the brown impurity was removed by washing with nitromethane, and the mauve crystals were dried *in vacuo;* yield 40%, m.p. 200.5°.

Anal. Calcd. for $C_{36}H_{30}CoN_2O_6P_2$: C, 61.12; H, 4.28; O, 13.57. Found: C, 60.87; H, 4.19; O, 13.15.

$Co\{(C_6H_5)_3AsO\}_2(NO_2)_2$ was obtained as mauve crystals by a method similar to that used for the previous compound; yield 50%, m.p. 183°.

Anal. Calcd. for $C_{36}H_{30}As_2CoN_2O_6$: C, 54.37; H, 3.80; N, 3.52; O, 12.07. Found: C, 53.76; H, 3.96; N, 3.51; O, 12.08.

Ni(tetmen)$(NO_2)_2$.[3]—A solution of nickel nitrite in methanol was prepared metathetically from sodium nitrite and nickel nitrate. The mixture was cooled in an acetone–solid CO_2 freezing mixture before filtering off the sodium nitrate. A four molar excess of tetmen was added to the nickel nitrite solution. Bright green crystals of the complex formed overnight and these were recrystallized from chloroform; yield 60%, m.p. 174°.

Anal. Calcd. for $C_6H_{16}N_4NiO_4$: C, 27.00; H, 6.04; N, 20.99; Ni, 21.99. Found: C, 27.36; H, 6.12; N, 20.46; Ni, 22.20.

Ni(α-picoline)$_2(NO_2)_2$ was obtained in 60% yield by a method analogous to that used for the previous compound. The green complex was recrystallized from α-picoline; on heating, the compound turns yellow at ~150° with decomposition.

Anal. Calcd. for $C_{12}H_{14}N_4NiO_4$: C, 42.77; H, 4.19; N, 16.63; O, 19.00. Found: C, 42.39; H, 4.17; N, 16.61; O, 19.20.

Ni(quinoline)$_2(NO_2)_2$ was prepared in 70% yield by a procedure similar to that described for the tetmen complex. The green complex was recrystallized from quinoline; m.p. 219° dec.

Anal. Calcd. for $C_{18}H_{14}N_4NiO_4$: C, 52.86; H, 3.45; N, 13.71. Found: C, 52.93; H, 3.63; N, 13.41.

Physical Measurements.—Magnetic susceptibility measurements were carried out on a Gouy balance of the conventional type. The electronic spectra of solutions of the complexes were obtained with a Perkin-Elmer Model 350 spectrometer, and those of the solid compounds were measured by the reflectance technique using Unicam S.P. 500 and Beckman DK2 spectrometers. Infrared spectra were obtained with a Grubb–Parsons Spectromaster grating spectrometer.

Molecular weights were determined with a Mechrolab, Inc., vapor pressure osmometer, Model 301A. The results are given in Table I.

The other complexes were either insoluble in or were quickly decomposed by solvents suitable for molecular weight determination.

TABLE I

Compound	Solvent	Concn., M	M_{obsd}	M_{calcd}
$Co\{(C_6H_5)_3PO\}_2(NO_2)_2$	Acetone	~0.01	793	795
$Co\{(C_6H_5)_3AsO\}_2(NO_2)_2$	Acetone	~0.01	725	708
Ni(tetmen)$(NO_2)_2$	$CHCl_3$	~0.05	270	267

Discussion

Several lines of evidence suggest that in the compounds $CoL_2(NO_2)_2$ (L = $(C_6H_5)_3PO$ or $(C_6H_5)_3AsO$) and $NiL_2(NO_2)_2$ (L = α-picoline or quinoline, or L_2 = tetmen[3]) the anions function as bidentate, chelating ligands.

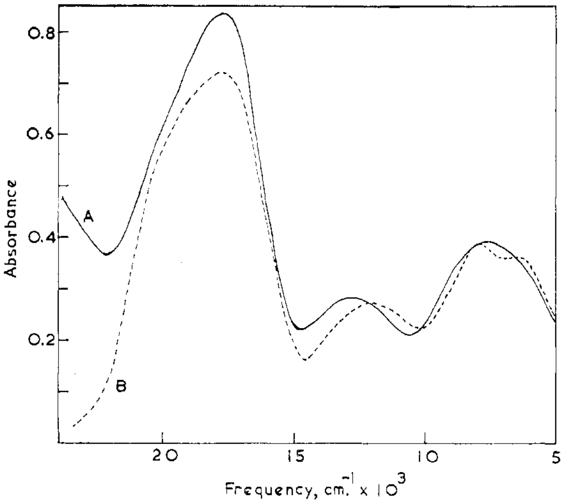

Figure 1.—Reflectance spectra of $Co\{(C_6H_5)_3AsO\}_2X_2$: A, X = NO_2^-; B, X = NO_3^-.

Cobalt Complexes.—X-Ray studies have shown[4] that the nitrate groups in $Co\{(CH_3)_3PO\}_2(NO_3)_2$ are bidentate, and similar structures have been suggested[5] for the corresponding compounds with triphenylphosphine oxide and triphenylarsine oxide. These cobalt nitrate complexes have rather distinctive electronic spectra,[5] with band intensities intermediate between those commonly found for octahedral and tetrahedral cobalt(II) complexes.

The electronic spectra of the solid cobalt(II) nitrite complexes were determined over the range 4000–30,000 cm.$^{-1}$ (Table II). They are very similar both in band position and band intensity to those of the analogous nitrate complexes (Figure 1). This close resemblance indicates that the ligand fields in the nitrite and nitrate complexes are essentially the same, and, therefore, that the cobalt(II) ions in the former are each surrounded by a distorted octahedron of oxygen atoms. Moreover, from the electronic spectra, it appears that the molecular structures of the cobalt nitrite complexes remain virtually unchanged on solution in acetone. However, these compounds are rather labile in solution, with either immediate or gradual formation of a brown color. Solutions in dry acetone remain without detectable decomposition for sufficient periods (~30 min.) to permit physical measurements to be carried out.

Although the electronic spectra suggest that both oxygen atoms of the NO_2 groups are coordinated to cobalt ions, this can be achieved either by chelation or by bridging. However, both compounds are monomeric in acetone, suggesting that in this solvent and in the solid state the nitrite groups are present as chelating ligands.

Further evidence in support of this is provided by the infrared absorption spectra of the compounds. Bands

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[3] tetmen = N,N,N′,N′-tetramethylethylenediamine.

[4] F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963).

[5] F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, **2**, 1162 (1963).

TABLE II

ELECTRONIC SPECTRA OF THE COMPLEXES

Compound	State	Absorption max., cm.$^{-1}$ (ϵ_{molar} for soln.)
$Co\{(C_6H_5)_3PO\}_2(NO_2)_2$	Solid	17,950,[a] 12,700, 7,400[b]
	Acetone (0.01 *M*)	~20,600 sh, 18,400 (80), 13,000 (2), 7,800[b] (8.5)
$Co\{(C_6H_5)_3AsO\}_2(NO_2)_2$	Solid	17,000,[a] 12,700, 7,870[b]
	Acetone (0.01 *M*)	17,450[a] (140), ~12,700 sh, 7,900[b] (14)
$Ni(tetmen)(NO_2)_2$	Solid	25,800, 15,900, 12,500,[c] 10,000, ~8,000 sh
	$CHCl_3$ (0.033 *M*)	25,800 (35), 15,850 (15), 10,000[b] (6.8)
$Ni(\alpha\text{-pic})_2(NO_2)_2$	Solid	24,600, 15,800, ~12,500 sh,[c] 8,700
$Ni(quinoline)_2(NO_2)_2$	Solid	24,500, 15,850, 8,850

[a] Band asymmetric to higher energy. [b] Band asymmetric to lower energy. [c] Very weak band assigned as spin-forbidden transition.

TABLE III

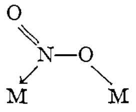
NO_2 FREQUENCIES (CM.$^{-1}$) FOR THE COMPLEXES

Compound[a]	Asymmetric N–O str., ν_{as}	Symmetric N–O str., ν_s	NO_2 deformation δ
$NaNO_2$[b]	1328 ± 2 m	1261 ± 3 vs	828 ms
$Co\{(C_6H_5)_3PO\}_2(NO_2)_2$	~1266[c] mw	1199 vs, 1176[c] vs	856 m
$Co\{(C_6H_5)_3AsO\}_2(NO_2)_2$	1314[c] mw	1193 vs, 1183 vs	847 m
$Ni(\alpha\text{-pic})_2(NO_2)_2$	1272 m	1199 s	866 w, 862 w
$Ni(quinoline)_2(NO_2)_2$	1299 m, 1289 m	1203 vs, 1193 vs	867 m
$Ni(tetmen)(NO_2)_2$ solid	1289[c] m	1200 vs	863[c] m
in CH_3CN	1284[c] m	1205 vs	862[c] m

[a] As Nujol and hexachlorobutadiene mulls unless stated otherwise. [b] From ref. 6. [c] Band not assigned with certainty due to organic ligand bands.

arising from the NO_2 groups are listed in Table III together with their assignments. These bands were identified by comparison of the spectra of the nitrite complexes with those of related compounds with halide anions.

Since the asymmetric (ν_{as}) and symmetric (ν_s) NO_2 stretches and NO_2 deformation (δ) of NO_2^- are nondegenerate modes the number of infrared bands arising from these does not change on coordination. However, shifts of ν_{as} and ν_s from the free-ion values have proved useful in determining the mode of coordination of the nitrite ion. In nitro complexes both ν_{as} and ν_s are raised in frequency,[7] while in nitrito complexes ν_{as} is increased while ν_s is lowered.[7,8] Although few data are available[1,7] for NO_2 groups acting as bridges, as in I, this mode of coordination appears to raise ν_{as} appreciably and to lower ν_s by a smaller amount. The



I

values of ν_{as} and ν_s observed for the cobalt nitrite complexes both fall below the free-ion values. This fact, especially the lowering of ν_{as}, suggests very strongly that the anions in these compounds are coordinated in a manner quite different from those in "nitrite" complexes of the types cited above. The ν_{as} and ν_s values are, in fact, in accord with the proposed mode of coordination as chelating groups. For an "ideal" model, in which both metal–oxygen bonds are equivalent, chelation would tend to retain the equivalence of the two N–O bonds while somewhat reducing their formal bond order, and hence the frequencies of ν_{as} and ν_s. This is somewhat similar to the effects observed for the C–O stretching frequencies of some compounds containing bridging carboxylates,[9] though for others, *e.g.*, $Cr_2(CH_3CO_2)_4 \cdot 2H_2O$,[10] the values of ν_{as} and ν_s (C–O) are very similar to those of the free ion.

The values of δ (NO_2) are all ~20–30 cm.$^{-1}$ higher than that of the free ion, whereas the frequencies reported[1,2,7,8] for the analogous mode for other types of "nitrite" complexes are generally little different from the free-ion value. The band due to ν_{as} (NO) in sodium nitrite is much weaker than that due to ν_s.[6,11] A similar relationship of band intensities is found for the chelating nitrite groups, whereas for nitro,[1,7] nitrito,[7,8] and M–N(O)O–M bridging[1,2] complexes the intensity of ν_{as} more nearly approaches that of ν_s.

The room-temperature magnetic moments of the two cobalt nitrite complexes (Table IV) are higher than those (~4.6 B.M.) of the analogous nitrate complexes.[5] In the case of $Co\{(CH_3)_3PO\}_2(NO_3)_2$ the arrangement of oxygen donor atoms is known to be quite irregular,[4] and an *essentially* similar geometry is to be expected for the other nitrate and the nitrite complexes. In these compounds the ground state, $^4T_{1g}$ in O_h symmetry, will be split into three orbital singlets, which will interact with levels of the same symmetry derived from O_h excited states. Therefore, the ground-state splitting, and hence the magnetic properties, depends upon the actual geometry of the primary coordination sphere and also upon the effective ligand fields generated by the oxygen atoms concerned. Thus differences

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(6) R. E. Weston and T. F. Brodasky, *J. Chem. Phys.*, **27**, 683 (1957).

(7) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York and London, 1963, pp. 151–155.

(8) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **3**, 1389 (1964).

(9) F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).

(10) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 4528 (1961).

(11) See ref. 7, p. 82.

Table IV

Magnetic Data for the Complexes

Compound	T, °K.	μ,[a] B.M.
$Co\{(C_6H_5)_3PO\}_2(NO_2)_2$	295	4.96 ± 0.05
$Co\{(C_6H_5)_3AsO\}_2(NO_2)_2$	295	5.03
$Ni(\alpha\text{-pic})_2(NO_2)_2$	294	3.28
$Ni(quinoline)_2(NO_2)_2$	294	3.29
$Ni(tetmen)(NO_2)_2$	294	3.37

[a] Calculated from the Curie law, using susceptibilities corrected for diamagnetism.

in the magnetic moments of the two groups of compounds might well be expected. The higher moments observed for the nitrite complexes suggest that the ligand fields in these are somewhat closer to octahedral than in the nitrates. It may be noted in this connection that the molar extinction coefficients of the bands at ~18,000 cm.$^{-1}$ in the electronic spectra of the nitrite complexes are appreciably smaller than those of the corresponding nitrates.

X-Ray powder photographs show that $Co\{(C_6H_5)_3AsO\}_2(NO_2)_2$ is not isomorphous with the corresponding nitrate.

Nickel Complexes.—Good evidence for the presence of chelating NO_2 groups in the nickel complexes is provided by their infrared spectra. The positions of ν_{as}, ν_s, and δ (NO_2) (see Table III) are quite comparable to those of the cobalt nitrite complexes, and the comments made for those apply here also.

The reflectance spectra of the complexes (Table II, Figure 2) are of the type commonly found for six-coordinate nickel(II). The highest and the lowest energy bands for the tetmen complex are at slightly higher energies than those of the other two compounds, but this can probably be attributed to a higher Δ value for tetmen than for the heterocyclic ligands.

The tetmen complex is quite stable in chloroform or acetone, and its electronic spectrum in the former solvent is virtually identical with that of the solid. Since the complex is monomeric in chloroform the attainment of six-coordination almost certainly results from the presence of chelating rather than bridging nitrite groups. The quinoline and α-picoline complexes were either insoluble in or were decomposed by common organic solvents, but the great similarity of their spectra (both infrared and electronic) to those of the tetmen complex suggests that they are of the same type. Moreover, the spectra of all these compounds are very similar to those reported[12] for $NiL_2(NO_3)_2$, L = 2,3-, 2,4-, and 2,5- lutidine, which are thought[12] to contain chelating nitrate groups.

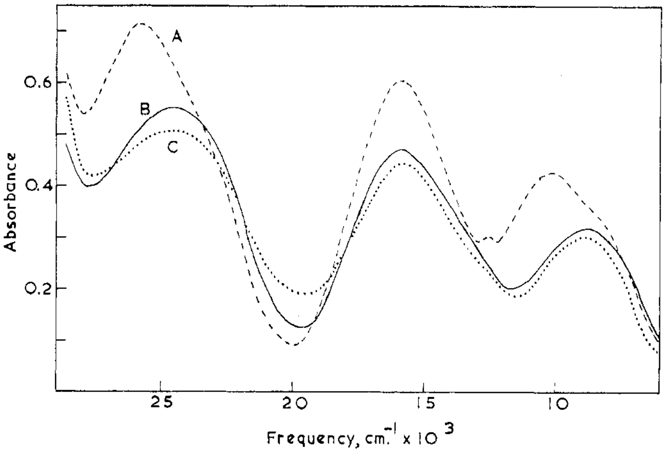

Figure 2.—Reflectance spectra of: A, $Ni(tetmen)(NO_2)_2$; B, $Ni(\alpha\text{-picoline})_2(NO_2)_2$; C, $Ni(quinoline)_2(NO_2)_2$.

General Comments.—The reasons for the adoption of the bidentate, chelating structure by the nitrite groups in the complexes described above are not completely clear. That NO_2^- should be able to coordinate in this way is not altogether surprising since both nitrate[13] and carboxylate ions[13,14] do this. What is less obvious is why it should bond in this manner in preference to the more usual methods. It has been suggested[13] that when oxy anions such as NO_3^- or RCO_2^- behave as bidentate, chelating ligands the mean positions of the pairs of oxygen donor atoms tend to lie approximately at the vertices of one of the common coordination polyhedra. If the NO_2^- ions in the nitrite complexes we have studied also follow this pattern, then the close similarity of the cobalt complexes with their nitrate analogs suggests that, *in this sense,* the coordination polyhedron concerned is the tetrahedron. It may be significant that the unidentate ligands L which give the complexes $ML_2(NO_2)_2$ with chelating NO_2 groups are reluctant to form compounds of stoichiometry ML_4X_2 with other cobalt(II) or nickel(II) salts, and the bis complexes ML_2X_2 are often pseudo-tetrahedral. Thus $(C_6H_5)_3AsO$ and $(C_6H_5)_3PO$ form tetrakis complexes only when the anions have poor coordinating ability, *e.g.,* I^- or ClO_4^-,[15,16] and the bis complexes with the metal halides are pseudo-tetrahedral.[16,17] Both quinoline[18] and α-picoline[19] form pseudo-tetrahedral complexes with nickel chloride and bromide, although the corresponding iodides are planar[18,20] and a polymeric, octahedral form of $Ni(quinoline)_2Cl_2$ is also known.[18] It is probable that in the case of quinoline, α-picoline, and tetmen the steric requirements of these ligands hinder the formation of stable nitrito complexes $NiL_4(ONO)_2$ or $Ni(diamine)_2(ONO)_2$ analogous to those described previously.[8] Steric reasons may also explain why nitrite bridges, such as those thought to be present in $Ni\{(C_2H_5)_2NCH_2CH_2NH_2\}(NO_2)_2$,[8] are not formed. Halide bridges in NiL_2X_2 are formed less readily when L is one of the more sterically hindered heterocyclic ligands.

The adoption of the chelating structure by the NO_2 groups in the nickel compounds may possibly be

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[12] S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 480 (1964).

[13] F. A. Cotton and J. G. Bergman, *J. Am. Chem. Soc.*, **86**, 2941 (1964), and references therein.

[14] J. H. Talbot, *Acta Cryst.*, **6**, 720 (1953); W. H. Zachariasen and W. A. Pettinger, *ibid.*, **12**, 526 (1959).

[15] E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1873, 1878 (1960).

[16] D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *Inorg. Chem.*, **1**, 239 (1962).

[17] F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **82**, 5771, 5774 (1960).

[18] D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.*, 207 (1963).

[19] M. D. Glonek, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **84**, 2014 (1962).

[20] W. Ludwig and G. Wittmann, *Helv. Chim. Acta*, **47**, 1265 (1964).

attributed to the tendency of nickel(II) to attain six-coordination, with more favorable bond energy resulting from the formation of four Ni–O bonds than from two $Ni-NO_2$ bonds. In contrast with this the anions in $Ni\{(n\text{-}C_4H_9)_3P\}_2(NO_2)_2$ are bonded through nitrogen.[21] However, nickel complexes with trialkylphosphines are usually diamagnetic *trans*-planar,[22] and the spin pairing would tend to favor $M-NO_2$ bonding, since nitro groups lie well toward the stronger end of the spectrochemical series, as compared with nitrito groups.

It is apparent from this and other recent work that the nitrite ion is a very versatile ligand and that further studies are necessary to elucidate the factors influencing its method of coordination.

Acknowledgment.—We thank the D.S.I.R. for a Research Studentship to M. A. H.

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[22] K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 265 (1936).

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Ligand Field Strength of the Nitrogen End of Cyanide and Structures of Cubic Cyanide Polymers[1]

BY D. F. SHRIVER, SHIRLEY A. SHRIVER, AND STANLEY E. ANDERSON[2]

Received November 12, 1964

Near-infrared, visible, and ultraviolet spectra were determined for potassium nickel ferrocyanide, potassium nickel cobalticyanide, and some related compounds. These materials involve Ni^{2+} octahedrally coordinated to the nitrogen end of cyanide, and straightforward analysis of the spectral data yields the ligand field strength for this ligand. The Dq value ranges between 1010 and 950 cm.$^{-1}$ and places the nitrogen end of cyanide below NH_3 on the spectrochemical series. The value of Dq noted above was used in an attempt to explain the structures of mixed cyanide polymers (*e.g.*, $KMnFe(CN)_6$) by calculation of site preference energies which were primarily based on crystal field stabilization energies. The site preference energies show a good correlation with actual structures. Linkage isomerism was predicted and found for $KFeCr(CN)_6$, which is less stable than $KCrFe(CN)_6$. The former compound apparently involves $Fe^{II}—N{\equiv}C—Cr^{III}$ linkages while the latter involves $Cr^{III}—N{\equiv}C—Fe^{II}$.

Introduction

Among the oldest known synthetic inorganic complexes are the cyanide polymers such as the Prussian blues. Keggin, Miles, and others have shown that these compounds occur with face-centered cubic lattices.[3] The structures involve transition metals in carbon and nitrogen octahedra. For example, recent studies on Prussian blue leave little doubt that Fe^{3+} is nitrogen-coordinated, while Fe^{2+} is carbon-coordinated.[4] Clearly, these polymeric cyanides afford a unique opportunity to study the behavior of the nitrogen end of cyanide as a ligand. It has not been possible to observe metal–$N{\equiv}C$ coordination in monomeric transition metal cyanide complexes because of the great affinity of these metals for the carbon end. Our objective was to determine the ligand field strength of the nitrogen end of cyanide, which is relevant to an understanding of structures of simple and polymeric cyanide complexes. Also, we were interested in comparing the spectra of polymeric cyanides with those of bridge addition compounds (*e.g.*, $K_4Fe(CNBF_3)_6$).[5]

Experimental

Analyses.—Before analysis samples were dried by gentle heating *in vacuo* and were subsequently handled in a water-free nitrogen atmosphere. Alkali metal was determined by Samuelson's ion-exchange procedure,[6] nickel gravimetrically as the dimethylglyoximate, and iron and chromium by modifications of published titrimetric procedures.[7] C, H, and N analyses were performed by Schwarzkopf Microanalytical Laboratory.

Spectroscopic Procedures.—Near-infrared, visible, and ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer. The mull transmittance technique was employed for Fluorolube or water suspensions of all samples.[8] In addition, most of the spectra were also determined by diffuse reflectance with the Cary integrating sphere attachment. Infrared spectra in the $C{\equiv}N$ stretch region were obtained on a prism-grating Beckman IR 9. The samples were in oil or water mulls.

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