CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
VICTORIA UNIVERSITY OF WELLINGTON, WELLINGTON, NEW ZEALAND

Some Nitrato-Amine Nickel(II) Compounds with Monodentate and Bidentate Nitrate Ions

BY N. F. CURTIS AND YVONNE M. CURTIS

Received December 14, 1964

The preparations of compounds of the types $Ni(en)_2(NO_3)_2$ and $[Ni(en)_2NO_3]ClO_4$ (en = ethylenediamine) and analogs with other diamines and with some cyclic tetramines are described. The infrared spectra of the nitrate ion for the two types of compound can be distinguished from each other, and from ionic nitrate, and are taken to indicate monodentate and bidentate nitrato groups, respectively. For $Ni(dien)(NO_3)_2$ (dien = diethylenetriamine) nitrato groups of both types are present while for one of the cyclic tetraminenickel(II) dinitrates, bidentate and ionic nitrates are present. The reflectance spectra of the dinitrato compounds are indicative of *trans* structures, while those of the mononitrato compounds resemble those of the known *cis* compounds $[Ni_2(en)_4Cl_2]Cl_2$ and $Ni(tren)(NCS)_2$ (tren = 2,2′,2″-triaminotriethylamine). The magnetic susceptibilities, all $\mu_{eff} \sim 3.1$ B.M., are reported.

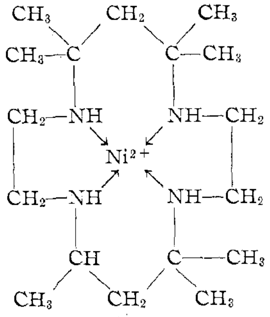
Introduction

The ability of the nitrate ion to act as a monodentate ligand in species such as $[Co(NH_3)_5NO_3]^{2+}$ is well established. Because the donor ability of nitrate is normally inferior to that of water, nitrato complexes of the labile M(II) ions have only recently been described. A series of compounds typified by $[(CH_3)_3PO]_2M(NO_3)_2$ (M = Co(II), Ni(II), Cu(II), and Zn(II)) has been reported,[1] and an X-ray crystallographic study of the Co(II) compound showed that each nitrate ion is acting as a bidentate coordinating agent, with two equivalent Co–O distances.[2] A series of tetranitrato complexes, $X_2[M(NO_3)_4]$, where M = Mn(II), Co(II), Ni(II), and Cu(II) and X is a large cation such as $(C_6H_5)_4As^+$, has been reported,[3] and a crystallographic investigation of the Co(II) compound again showed the presence of bidentate nitrato groups, although this time the Co–O distances are nonequivalent.[4] In view of the similarities in preparation and properties it is reasonable to suppose the Ni(II) nitrato compounds have structures similar to their Co(II) analogs. The structures of other compounds with bidentate nitrate have been described.[2] Structures with bidentate nitrate groups have been proposed for Ni(II) complexes with some substituted pyridines.[5] In this paper the preparation and properties of two series of nitrato tetraminenickel(II) compounds are described. On the basis of visible and infrared spectroscopic measurement, structures are postulated for one series with monodentate nitrate, and for the other series with bidentate nitrate.

Experimental

Commercial ethylenediamine (en), diethylenetriamine ($(NH_2\text{-}CH_2CH_2\text{-})_2NH$, dien), and 1,3-propanediamine (trimethylenediamine, tmd) were used without further purification. A general preparation of the amine compounds was to add the calculated amount of amine to a hot methanol solution of nickel nitrate hexahydrate for the dinitrato compounds, or a hot methanol solution of equimolar amounts of hexahydrated nickel nitrate and perchlorate for the nitratoperchlorate compounds. The resultant solution was quickly filtered while hot before the product nucleated, and the product was filtered from the cold solution, washed with methanol, and vacuum dried. The compounds were also prepared by mixing the hexaminenickel salts and nickel nitrate and/or perchlorate in hot methanol to obtain the correct mole ratio of nickel:amine:nitrate:perchlorate. The fluoroborate $[Ni(en)_2NO_3]BF_4$ was prepared by the first method, substituting nickel fluoroborate for the nickel perchlorate. The iodide $[Ni(en)_2NO_3]I$ crystallized when NaI was added to a solution of $Ni(en)_2(NO_3)_2$ in hot methanol (1:1 mole ratio). Evaporation of an aqueous solution of the dinitrate $Ni(en)_2(NO_3)_2$ yielded the dihydrate $[Ni(en)_2(H_2O)_2](NO_3)_2$.[6] The water is readily lost on exposure to the air.

The (cyclic tetramine)nickel(II) cations $[Ni(tet\ a)]^{2+}$ and $[Ni(tet\ b)]^{2+}$ (I) were prepared as previously described.[7] The isomers tet *a* and tet *b* are probably the *racemic* and *meso* modifications. Details of the preparation of the nitrato compounds by metathetical reactions from the perchlorates will be given in papers dealing with the properties of the compounds of these cations. (Briefly, the dinitrates are precipitated from aqueous solutions of the chlorides by sodium nitrate, while $[Ni(tet\ b)NO_3]ClO_4$ crystallizes when sodium nitrate is added to an aqueous solution of the perchlorate.) The color and analytical data for the compounds are reported in Table I.



I

Infrared spectra were measured using a Perkin-Elmer Model 221 spectrophotometer with NaCl-grating optics, using mulls in Nujol and hexachlorobutadiene. Reflectance spectra were measured using a Unicam SP 700 recording spectrophotometer

---

[1] E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 2276 (1960); F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, **2**, 1162 (1963).

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

[3] D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, **1**, 848 (1962).

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

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

[6] T. Inoue, *J. Chem. Soc. Japan*, **54**, 65 (1933).

[7] N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

TABLE I

ANALYTICAL DATA

Compound	Color	Ni, %[a] Found	Ni, %[a] Calcd.	C, %[b] Found	C, %[b] Calcd.	H, %[b] Found	H, %[b] Calcd.	Equiv. wt.[c] Found	Equiv. wt.[c] Calcd.
$[Ni(en)_3](NO_3)_2$	Violet	16.1	16.2					60.5	60.5
$[Ni(dien)_2](NO_3)_2$	Violet	15.1	15.1[d]	24.8	24.7	6.9	6.7		
$[Ni(tmd)_2(H_2O)_2](NO_3)_2$	Blue-violet	15.8	16.0	19.7	19.6	6.3	6.5	91	92
$Ni(en)_2(NO_3)_2$	Violet	19.4	19.4	16.0	15.8	5.3	5.3	77	76
Ni(tet *a*)$(NO_3)_2$	Violet	12.5	12.6[d]	40.8	41.1	8.0	7.8		
$[Ni(en)_2NO_3]ClO_4$	Blue	17.5	17.2	14.5	14.1	4.8	4.7	84	85
$[Ni(en)_2NO_3]BF_4$	Blue	17.9	17.9	15.1	14.7	5.4	4.9		
$[Ni(en)_2NO_3]I$	Blue	16.1	16.0	13.3	13.0	4.8	4.5		
$[Ni(tmd)NO_3]ClO_4$	Blue	15.8	15.9	19.8	19.6	5.8	5.4	93	92
[Ni(tet *b*)$NO_3]ClO_4\cdot{}^1/_2H_2O$[e]	Lilac	11.5	11.4	37.7	37.4	7.9	7.3		
$Ni(dien)(NO_3)_2$	Turquoise blue	20.2	20.5[d]	16.9	16.8	5.1	4.6		
[Ni(tet *b*)$NO_3]NO_3$	Lilac	12.6	12.6[d]	41.1	41.1	7.7	7.8		

[a] Determined gravimetrically, using dimethylglyoxime. [b] C and H microanalyses by Dr. A. D. Campbell, Otago University. [c] Weight reacting with one mole of acid, determined by pH titration; addition of excess standard acid, and back titration to a predetermined end point with standard alkali. [d] Complex decomposed by boiling peroxydisulfate. [e] Calcd.: N, 13.6. Found: N, 13.6.

with $MgCO_3$ as reference. X-Ray powder diffraction was measured using a Philips recording diffractometer. Magnetic susceptibility measurements were made using the Gouy method, with $Ni(en)_3S_2O_3$ as calibrant.[8]

Results

Infrared Spectra.—The infrared spectrum of the nitrate ion in "ionic" compounds (D_{3h} symmetry) shows three bands, ν_2 (out-of-plane deformation), ν_3 (doubly degenerate stretch), and ν_4 (doubly degenerate in-plane bending). ν_1 (symmetric stretch) is normally inactive, but sometimes becomes weakly active through crystal interactions. The infrared spectrum of coordinated nitrate has previously been described.[5,9–11] When the nitrate ion acts as a monodentate coordinating agent (C_{2v} symmetry) all bands become active, shifts in band positions occur, and the degeneracy of ν_3 and ν_4 is lifted.

The symmetry remains C_{2v} for bidentate coordination, but band positions may be altered compared with monodentate nitrate compounds. With CO_3^{2-}, which is known to act as a monodentate and as a bidentate ligand, the band splittings and shifts for the bidentate coordination are similar to but larger in magnitude than those for monodentate coordination (Figure 1). The infrared spectra of the nickel–amine–nitrate compounds are shown in Table II. The coordinated amines have a complex spectrum which sometimes prevented positive identification of the bands due to nitrate, particularly in the region of ν_1. The compounds fall into three groups:

(1) **Compounds with Ionic Nitrate.**—The compounds $[Ni(en)_3](NO_3)_2$ and $[Ni(dien)_2](NO_3)_2$, with six amine donor groups, and the dihydrates $[Ni(en)_2(H_2O)_2](NO_3)_2$ and $[Ni(tmd)_2(H_2O)_2](NO_3)_2$ have nitrate spectra characteristic of ionic nitrate.

(2) **Compounds with Monodentate Nitrate.**—The compounds $Ni(en)_2(NO_3)_2$ and Ni(tet *a*)$(NO_3)_2$ have magnetic moments ($\mu_{eff} \sim 3.1$ B.M.) characteristic of approximately octahedral Ni(II) with triplet ground state and absorption spectra characteristic of tetragonally distorted octahedral Ni(II) with triplet ground state. With four amine coordinating groups monodentate nitrate coordination is indicated. The infrared spectra of the nitrate ions are similar for the compounds, the main differences from the ionic compounds being considerable weakening of ν_3, splitting of ν_3 and ν_4, and a small shift of ν_2 to lower frequency.

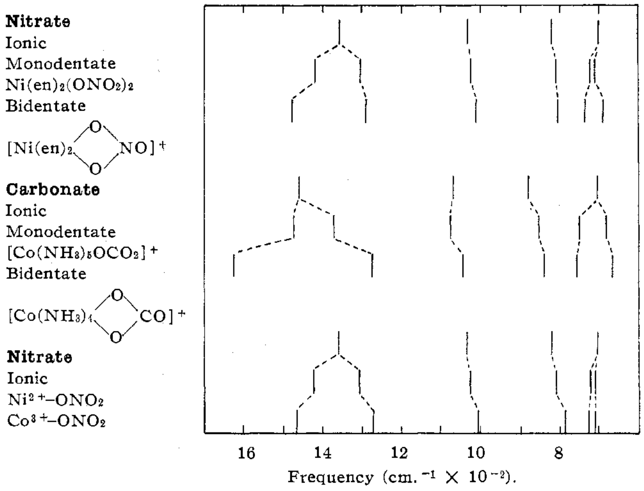


Figure 1.—Infrared spectral band positions.

(3) **Compounds with Bidentate Nitrate.**—The compounds $[Ni(en)_2NO_3]X$ ($X = ClO_4^-, BF_4^-, I^-$), $[Ni(tmd)_2NO_3]ClO_4$, and [Ni(tet *b*)$NO_3]ClO_4\cdot{}^1/_2H_2O$ have nitrate spectra similar to those of known chelate nitrato compounds and distinguishable from the class 2 compounds. The infrared spectra of the perchlorate and tetrafluoroborate ions show no indication of coordination. With four coordinating amine groups, the nitrate ions must be bidentate for the nickel to achieve octahedral coordination as indicated by the magnetic susceptibility and absorption spectra.

The chain polymeric structure $-(en)_2Ni-O(NO)O-Ni(en)_2-$ (analogous to $Ni(en)_2NO_2ClO_4$ with $-(en)_2Ni-O(NO)-Ni(en)_2-$ chains)[12] is compatible with the infra-

---

(8) N. F. Curtis, *J. Chem. Soc.*, 3147 (1961).

(9) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *ibid.*, 4222 (1957); *J. Inorg. Nucl. Chem.*, **8**, 75 (1958).

(10) C. C. Addison and B. M. Gatehouse, *J. Chem. Soc.*, 613 (1960); B. M. Gatehouse and A. E. Comyns, *ibid.*, 3965 (1958).

(11) E. P. Bertin, R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 3818 (1959).

(12) F. J. Llewellyn and T. N. Waters, *J. Chem. Soc.*, 3845 (1962).

TABLE II

INFRARED SPECTRA (FUNDAMENTAL ABSORPTION BONDS OF THE NITRATE ION, CM.$^{-1}$)[a]

Compound	ν_2	ν_3	ν_4
Ionic nitrate			
$[Ni(en)_3](NO_3)_2$	823 m, sp	1368 vs, br	704 w, sp
$[Ni(dien)_2](NO_3)_2$	823 m, sp	1365 vs, br	707 w, sp
$[Ni(en)_2(H_2O)_2](NO_3)_2$	821 m, sp	1368 vs, br	702 w
$[Ni(tmd)_2(H_2O)_2](NO_3)_2$	817 m, sp	1355 vs, br	718 w (?)[b]
Monodentate nitrate			
$Ni(en)_2(NO_3)_2$	818 m, sp	1305 s, 1420 s	708 w, sp, 728 w, sp
$Ni(tet\ a)(NO_3)_2$	817 m, sp	1307 s, 1412 s	708 w, sp, 721 vw
$[Co(en)_2(NO_3)_2]ClO_4$	796 m	1278 s, 1478 s	734 w, br, 720 vw, sh(?)
Bidentate nitrate			
$[Ni(en)_2NO_3]ClO_4$	809 m, sp	1290 s, 1476 s[c]	695 vw, 746 w, sp
$[Ni(en)_2NO_3]BF_4$	807 m, sp	1290 s, 1475 s[c]	695 vw, 743 w, sp
$[Ni(en)_2NO_3]I$	805 m, sp	1292 s, 1480 s[c]	702 vw, 740 w, sp
$[Ni(tmd)_2NO_3]ClO_4$	810 m, sp	1250 s, sp, 1485 s	698 vw, 740 w, sp
$[Ni(tet\ b)NO_3]ClO_4$	802 m, sp	1263 s, sp, 1493 s	696 vw, 740 w, sp
Mono- and bidentate nitrate			
$Ni(dien)(NO_3)_2$			
Monodentate nitrate	816 m, sp	1315 s, 1440 s[b]	714 vw, sp, 736 w, sp
Bidentate nitrate	808 m, sp	1300 s, 1480 s[b]	698 vw, sp, 749 w, sp
Ionic and bidentate nitrate			
$[Ni(tet\ b)NO_3]NO_3$			
Ionic nitrate	825 m, sp	1375 s, br	704 w, sp
Bidentate nitrate	806 m, sp	1280 s, 1490 s	695 vw, 745 w, sp

[a] ν_1, which should become infrared active on coordination, remains weak, or inactive, and could not be distinguished among the many amine bands in the expected region. [b] This may be an amine band. [c] This band occurs as a shoulder on a more intense amine band.

red spectra. However, the nickel ion d–d spectrum would be expected to be similar to that of the other *trans* compounds (*e.g.*, $Ni(en)_2(NO_3)_2$) instead of being similar to that of the *cis* compound $Ni(en)_2Cl_2$, as observed. The similarity of the compounds $[Ni(en)_2X]ClO_4$, where X = NO_3^-, CH_3COO^-, and $^1/_2C_2O_4^{2-}$,[13] also renders the chain structure improbable. Arrangements with bridging acetate and nitrate are possible, but one with each oxygen atom of an oxalate ion interacting with a different $[Ni(en)_2]^{2+}$ ion is structurally improbable.

Five-coordinate structures with monodentate nitrate are considered improbable for these compounds since: (i) five-coordinate structures are very uncommon for Ni(II), (ii) the infrared spectrum of the nitrate ion is distinguishable from those of the other monodentate nitrates and resembles those of known chelate nitrates,[1] (iii) the similarity to the acetato and oxalato compounds[13] above, for which the infrared spectra indicate equivalent C–O bonds.

The infrared spectra of the nitrate ion for these compounds show a greater weakening of ν_3, greater splittings of ν_3 and ν_4, and a larger shift of ν_2 to lower frequency than observed for the class 2 compounds.

The compound $Ni(dien)(NO_3)_2$ has three amine coordinating sites and the octahedral coordination indicated by the magnetic susceptibility and the absorption spectrum would be achieved with one monodentate and one bidentate nitrate ion. The infrared spectrum shows bands characteristic of both class 2 and class 3 compounds, ν_3 and ν_4 being split into four and ν_2 into two bands.

The dinitrate of $[Ni(tet\ b)]^{2+}$ has a nitrate spectrum characteristic of both ionic and bidentate nitrate, and hence the compound is formulated as $[Ni(tet\ b)NO_3]NO_3$, analogous to the nitrate perchlorate. The differences between the spectrum of this compound and those of the other dinitrato compounds are unambiguous and clearly indicate structural differences, thus supporting the formulation of the other dinitrato compounds.

Figure 1 shows a diagrammatic representation of the infrared spectra of the Ni(II) amine compounds with ionic nitrate and mono- and bicoordinate nitrato groups. For comparison the spectra of the carbonate ion in analogous Co(III) compounds are included. A similar figure published earlier[1] is less conclusive in that the monodentate nitrate is coordinated to Co(III) (in, *e.g.*, $[Co(NH_3)_5NO_3]^{2+}$), while the bidentate nitrate species is coordinated to Co(II) (in $((CH_3)_3PO)_2Co(NO_3)_2$). The changes in the spectrum of nitrate coordinated to a M(II) ion are qualitatively similar to, but smaller than, those of the nitrate ion coordinated to a M(III) ion. In the tables, the nitrate spectrum of $[Co(en)_2(NO_3)_2]ClO_4$ is reported. This is very similar to that of $[Co(NH_3)_5NO_3]Cl_2$, reported by Bertin, *et al.*,[11] except that the ν_4 and the combination bands were observed. The bands of ionic nitrate and monodentate nitrate coordinated to Ni(II) and Co(III) are represented schematically in Figure 1.

---

(13) N. F. Curtis, *J. Chem. Soc.*, 4109 (1963).

TABLE III

INFRARED SPECTRA (OVERTONE AND COMBINATION BANDS OF THE NITRATE ION, CM.$^{-1}$)

Compound	$\nu_1 + \nu_3$	Δ	$\Delta\nu_3$	ν_1 (calcd.)	$\nu_1 + \nu_4$	Δ	$\Delta\nu_4$	ν_1 (calcd.)	$2\nu_1$	ν_1 (calcd.)
Ionic nitrate										
$[Ni(en)_3](NO_3)_2$	2380	...	...	1022	1750	...	...	1046	2065[a]	1032
$[Ni(dien)_2](NO_3)_2$	2405	...	...	1040	1753	...	...	1046	2070[a]	1035
$[Ni(en)_2(H_2O)_2](NO_3)_2$	2405	...	...	1037	1773	...	...	1071	2070[a]	1035
$[Ni(tmd)_2(H_2O)_2](NO_3)_2$	2415	...	...	1060	1768	...	...	1050	2075[a]	1037
Monodentate nitrate										
$Ni(en)_2(NO_3)_2$	2320, 2455	135	115	1015, 1035	1741, 1762	21	20	1033, 1034	2070	1035
$Ni(tet\ a)(NO_3)_2$	2330, 2445	115	105	1023, 1033	1752, 1768	16	13	1044, 1047	2085	1042
$[Co(en)_2(NO_3)_2]ClO_4$	2300, 2490	190	200	1012, 1022	1735, (1720?)	(15?)	(14?)	1011, 1000	2015	1008
Bidentate nitrate										
$[Ni(en)_2NO_3]ClO_4$	2300, 2500	200	186	1010, 1025	1725, 1771	46	51	1030, 1025	2050[a]	1025
$[Ni(en)_2NO_3]BF_4$	2300, 2500	200	185	1010, 1025	1726, 1770	44	48	1031, 1027	2055	1027
$[Ni(en)_2NO_3]I$	2315,[a] 2505	190	188	1023, 1025	1728, 1773	45	38	1026, 1033	2070[a]	1035
$[Ni(tmd)_2NO_3]ClO_4$	2305, 2515	210	235	1055, 1030	1728, 1769	41	42	1030, 1029	2010	1005
$[Ni(tet\ b)NO_3]ClO_4$	2275, 2520	245	230	1012, 1027	1715, 1768	53	44	1019, 1028	2020	1010
$Ni(dien)(NO_3)_2$										
Monodentate nitrate	2315, 2465	150	125	1000, 1025	1738, 1748	10	22	1036, 1036	2070	1035
Bidentate nitrate	2315, 2475	160	180	1015, 995	1734, 1785	51	51	1024, 1012	2020[a]	1010
$[Ni(tet\ b)NO_3]NO_3$										
Ionic nitrate	2400	...	...	1025	1752	...	...	1048	2055	1027
Bidentate nitrate	2295, 2515	220	210	1015, 1025	1724, 1770	46	55	1029, 1015	2055	1027

[a] Assignment of these bands is somewhat uncertain.

Overtone and Combination Bands (Table III).—The infrared spectra of many nitrate compounds show several weak bands in the region 2500–1700 cm.$^{-1}$. One band near 2400 cm.$^{-1}$ for the ionic nitrates occurs as a doublet of separation similar to the spacing of the ν_3 doublet for nitrato compounds. If the band is assumed to be a $(\nu_1 + \nu_3)$ combination, a reasonable value is calculated for ν_1. Similarly a single band near 1750 cm.$^{-1}$ for the ionic nitrates becomes a doublet of separation similar to that of the ν_4 doublet for the nitrato compounds, and assignment as $(\nu_1 + \nu_4)$ gives a similar value for ν_1. Another band near 2050 cm.$^{-1}$ remains single for the nitrato compounds, and the assumption that this is $2\nu_1$ gives a similar value for ν_1. The values of ν_1 obtained from the three bands are in reasonable, but not exact, agreement. $Ni(dien)(NO_3)_2$ shows bands in this region supporting the formulation with both mono- and bidentate nitrato groups, while the spectrum of $[Ni(tet\ b)NO_3]NO_3$ indicates the presence of ionic and bidentate nitrate groups. The intensity of the bands $(\nu_1 + \nu_4)$ and $(\nu_1 + \nu_3)$ decreases in the order ionic, monodentate, and bidentate nitrate, while the intensity of the $2\nu_1$ band is greatest for the bidentate nitrate. Similar overtone and combination bands were observed for $[Co(en)_2(NO_3)_2]ClO_4$ (Table III). The occurrence of some of these weak bands for ionic nitrate has previously been reported,[14] and for coordinated nitrate some assignments as overtones and combination bands have been made.[10]

The nitrate perchlorate of $[Ni(tet\ b)]^{2+}$ is formulated as a hemihydrate because the infrared spectrum shows weak sharp bands at 3610 and 3525 cm.$^{-1}$ and a weak broad band at ~1640 cm.$^{-1}$. The frequencies and sharpness of the bands are characteristic of lattice rather than coordinated or strongly H-bonded water. The analytical data fit best for the hemihydrate. Similar water bands occur for the analogous compounds $[Ni(tet\ b)CH_3COO]ClO_4 \cdot {}^1/_2H_2O$ and $[Ni(tet\ b)BH_4]ClO_4 \cdot {}^1/_2H_2O$,[15] and again the analytical data fit best for the hemihydrates.

Reflectance Spectra.—The reflectance spectra (Table IV and Figure 2) of the hexamines $[Ni(en)_3](NO_3)_2$ and $[Ni(dien)_2](NO_3)_2$ show the three bands (ν_1, ${}^3A_{2g} \rightarrow {}^3T_{2g}$; ν_2, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$; ν_3, ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$) characteristic of triplet ground-state Ni(II) with octahedral coordination. Replacement of two amine groups, most probably *trans*, by water molecules in $[Ni(en)_2(H_2O)_2](NO_3)_2$, with consequent tetragonal distortion of the ligand field, results in the splitting of ν_1, as observed[16] for $Ni(py)_4Cl_2$ with known *trans* structure.[17] The dinitrate tetramine compounds have spectra similar to those of the diaquo compounds. (A series of compounds $Ni(tet\ a)X_2$, to be described subsequently, has been prepared, and these show similar spectra, with a ν_1 split indicating tetragonal structures. The values for $X = NO_3^-$, Cl^-, and CH_3COO^- are listed in Table IV.)

---

(14) F. A. Millar and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952); M. Anbar, M. Halmann, and S. Pinchas, *J. Chem. Soc.*, 1242 (1960).

(15) N. F. Curtis, *ibid.*, 924 (1965).

(16) O. Bostrup and C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 1223 (1957).

(17) The *trans* structure has been generally found for compounds of the type NiL_4X_2 (*e.g.*, $Ni(py)_4Cl_2$,[18] $Ni(py)_4Br_2$[19] (py = pyridine), $Ni(en)_2(NCS)_2$,[20] $Ni(NH_3)_4(NCS)$,[19] $Ni(NH_3)_4(ONO)_2$,[19] $Ni(en)_2ONOClO_4$ (with bridging ONO groups),[12] some Lifschitz salts,[21] $Ni(thiourea)_4Cl_2$[22]). The *cis* structure has been observed for $Ni(en)_2Cl$,[23] $Ni(en)_2Br_2$,[23] and $Ni(tren)(NCS)_2$[24] (tren = 2,2′,2′′-triaminotriethylamine).

(18) M. A. Porai-Koshits, *Dokl. Akad. Nauk SSSR*, **92**, 333 (1953); *Chem. Abstr.*, **48**, 3838 (1954).

(19) M. A. Porai-Koshits, A. S. Antsyshkina, L. M. Dichareva, and E. K. Jukhov, *Acta Cryst.*, **10**, 784 (1957); M. A. Porai-Koshits and L. M. Dichareva, *Kristallografiya*, **4**, 650 (1959).

(20) B. W. Brown and E. C. Lingafelter, *Acta Cryst.*, **16**, 753 (1963).

(21) S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, **3**, 468 (1964).

(22) A. L. Castro and M. R. Truter, *J. Chem. Soc.*, 1309 (1963).

(23) A. S. Antsyshkina and M. A. Porai-Koshits, *Dokl. Akad. Nauk SSSR*, **143**, 105 (1963); *Chem. Abstr.*, **57**, 2954 (1962).

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

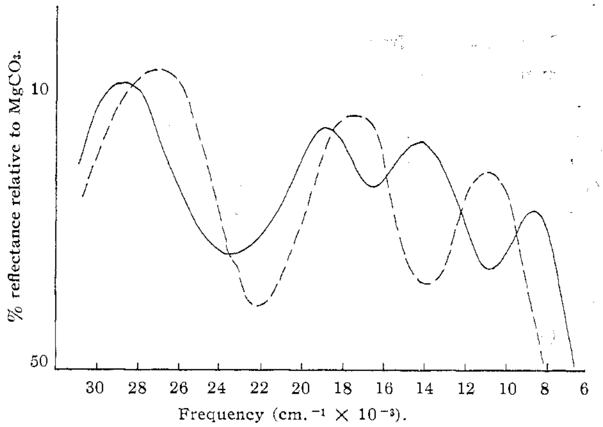


Figure 2.—Typical reflectance spectra: solid curve (a) $Ni(en)_2(NO_3)_2$; dashed curve (b) $[Ni(en)_2NO_3]ClO_4$.

The extent of the splitting of ν_1 gives a measure of the tetragonal distortion of the ligand field, *i.e.*, the extent to which the ligand field strength of the axial ligands differs from that of the equatorial amine groups.[25] From the data in Table IV, the ligand field strength order is en $> NO_3^- > H_2O$ for $Ni(en)_2X_2$ and tet *a* $> CH_3COO^- > NO_3^- > Cl^-$ for $Ni(\text{tet } a)X_2$, in line with the accepted order.

Table IV

Reflectance Spectra (cm.$^{-1}$ × 10^{-3})

Compound	ν_1		ν_2	ν_3
Ionic nitrate				
$[Ni(en)_3](NO_3)_2$	11.3		18.3	28.8
$[Ni(dien)_2](NO_3)_2$	11.3		19.1	27.9
$[Ni(en)_2(H_2O)_2](NO_3)_2$	8.8	14.6	18.1	27.4
$[Ni(tmd)_2(H_2O_2](NO_3)_2$	8.3	13.1	17.5	27.9
Monodentate nitrate				
$Ni(en)_2(NO_3)_2$	8.7	14.1	18.4	28.8
$Ni(\text{tet } a)(NO_3)_2$	8.1	15.7	19.0	28.7
Bidentate nitrate				
$[Ni(en)_2NO_3]ClO_4$	10.6		17.5	27.3
$[Ni(en)_2NO_3]BF_4$	10.5		17.5	27.2
$[Ni(en)_2NO_3]I$	10.8		17.7	27.8
$[Ni(tmd)_2NO_3]ClO_4$	10.4		17.1	26.9
$[Ni(\text{tet } b)NO_3]ClO_4 \cdot {}^1/_2H_2O$	10.7		17.5	27.6
Mono- and bidentate nitrate				
$Ni(dien)(NO_3)_2$	10.4		16.6	26.7
Ionic and bidentate nitrate				
$[Ni(\text{tet } b)NO_3]NO_3$	10.5		17.4	27.4
Other compounds				
$Ni(tren)(NCS)_2$[a]	10.9		17.9	27.8
$[Ni_2(en)_4Cl_2]Cl_2$	10.2		16.9	26.9
$[Ni(en)_2(C_2O_4)_{0.5}]ClO_4$	11.0		17.4	28.0
$[Ni(\text{tet } b)(C_2O_4)_{0.5}]ClO_4$	10.3		17.2	27.3
$[Ni(en)_2CH_3COO]ClO_4$	10.6		17.6	27.8
$Ni(py)_4Cl_2$[a]	8.5	10.9	15.9	25.7
$Ni(\text{tet } a)Cl_2$	8.1	14.3	18.4	28.0
$Ni(\text{tet } a)(CH_3COO)_2$	9.6	13.4	18.4	28.8

[a] O. Bostrop and C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 1223 (1957).

The spectra of $Ni(en)_2Cl_2$, known to have the *cis* dichloro bridged structure $[(en)_2NiCl_2Ni(en)_2]Cl_2$,[23] and $Ni(tren)(NCS)_2$, also known to have a *cis* structure,[24] are similar to that of an octahedral complex such as $[Ni(en)_3]^{2+}$, but with lower average ligand field strength. The spectra of the chelate nitro, acetato, oxalato, etc., compounds are similar to that of $Ni(en)_2Cl_2$, quite unlike those of the dinitrato compounds (Figure 2). The deviation of the ligand field from octahedral symmetry in these cases must be considerable, since as well as the difference between the ligand field strengths of the amine and anion (as for $Ni(en)_2Cl_2$), there will be considerable geometrical distortion from an octahedral arrangement. (The OCoO angle observed for $((CH_3)_3PO)_2Co(NO_3)_2$ is 57.2°.[2]) The spectrum of $Ni(dien)(NO_3)_2$ resembles that of the chelate nitrato compounds.

Magnetic Susceptibilities.—The magnetic susceptibilities of several of the nitrato derivatives were measured to see if the differing distortions of the ligand field for the mono- and bidentate compounds produced any change in the orbital contributions to the susceptibilities. The values obtained for the magnetic moment (Table V) are all close to 3.1 B.M., indicating no significant effect.

Table V

Magnetic Susceptibilities

Compound	T, °K.	χ_g × 10^5	χ_m × 10^6	Diam. cor.	$\chi_{m,cor}$ × 10^6	μ_{eff}, B.M.[a]
$[Ni(dien)_2](NO_3)_2$	294	9.89	3849	176	4025	3.09
$Ni(en)_2(NO_3)_2$	293	12.73	3856	123	3979	3.06
$Ni(\text{tet } a)(NO_3)_2$	287	8.57	4005	271	4276	3.15
$[Ni(en)_2NO_3]ClO_4$	292.5	11.54	3928	137	4065	3.10
$[Ni(tmd)_2NO_3]ClO_4$	292	11.21	4131	183	4314	3.19
$[Ni(\text{tet } b)NO_3]ClO_4 \cdot {}^1/_2H_2O$	291	7.34	3770	90	4060	3.09
$Ni(dien)(NO_3)_2$	294.5	14.35	4102	131	4233	3.17

[a] $2.84(\chi_{m,cor}T)^{1/2}$.

X-Ray Powder Diffraction.—The diffraction patterns of $[Ni(en)_2NO_3]ClO_4$, $[Ni(en)_2NO_3]BF_4$, and $[Ni(en)_2CH_3COO]ClO_4$ are very similar, with all major lines in common, indicating that the compounds are isostructural. The pattern of $[Ni(en)_2NO_3]I$ has many lines in common with the above compounds and it is probably isostructural. Similarly, $[Ni(\text{tet } b)NO_3]ClO_4 \cdot {}^1/_2H_2O$ and $[Ni(\text{tet } b)CH_3COO]ClO_4 \cdot {}^1/_2H_2O$ are probably isostructural and definitely different from $[Ni(\text{tet } b)NO_3]NO_3$. The dinitrates of $[Ni(\text{tet } a)]^{2+}$ and $[Ni(\text{tet } b)]^{2+}$ are structurally dissimilar, lending support to the formulations as $Ni(\text{tet } a)(NO_3)_2$ and $[Ni(\text{tet } b)NO_3]NO_3$, respectively.

Properties in Solution.—Solutions of $[Ni(en)_2NO_3]ClO_4$, $Ni(en)_2(NO_3)_2$, and $[Ni(en)_2](ClO_4)_2$ in methanol were found to have identical spectra, indicating dissociation of the nitrate ion with formation of the disolvate. The compound $Ni(\text{tet } a)(NO_3)_2$ is insoluble in organic solvents and dissolves in water to give an orange solution, the visible spectrum showing the single band at 21,650 cm.$^{-1}$ characteristic of singlet ground state $[Ni(\text{tet } a)]^{2+}$.[7] $[Ni(\text{tet } b)NO_3]ClO_4$ dissolves in water and many organic solvents to form a blue-violet solution, indicating incomplete nitrate dissociation. (The properties of these solutions will be described in a later publication dealing with the properties of $[Ni(\text{tet } b)]^{2+}$ compounds in general.)

---

(25) C. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 792 (1964).

Discussion

Bis(ethylenediamine)nickel(II) compounds can occur with octahedrally coordinated nickel(II), with *trans* (*e.g.*, $Ni(en)_2(NO_3)_2$) or with *cis* (*e.g.*, $[Ni(en)_2NO_3]ClO_4$, $[Ni_2(en)_4Cl_2]Cl_2$,[21] $[Ni(en)_3]^{2+}$) arrangements. With two coordinated anions, the *trans* is the usual arrangement,[17] as this minimizes inter-ligand repulsion. Thus bis(ethylenediamine)nickel(II) nitrate crystallizes from methanol as the *trans* dinitrato compound with monodentate nitrates, $Ni(en)_2(NO_3)_2$. The addition of appropriate other anions (*e.g.*, ClO_4^-, BF_4^-, I^-) to the methanol solutions causes the crystallization of the chelate mononitrato compounds $[Ni(en)_2NO_3]X$, indicating comparable stabilities for the monodentate dinitrato and chelate mononitrato forms in the solid state. (There is no evidence that either occurs in solution.) This suggests that the greater crystal energy of the ionic chelated form $[Ni(en)_2NO_3]X$, where X is an appropriately sized anion, may be the most important factor causing the crystallization of this form. Another factor favoring this form will be the reduced interligand repulsion energy with only one coordinated anion and with the spreading of the amine groups to take advantage of the small angle subtended in the coordination sphere by the chelate nitrate ion (compare[2] $Co\{(CH_3)_3PO\}_2(NO_3)_2$, OCoO angle 57.2°). The crystallization of the chelate mononitrate compound from solutions containing excess nitrate suggests that the energy of interaction of the nickel(II) ion with the two oxygen atoms of a chelate nitrate is not much smaller than that for the interaction with two *trans* monodentate nitrates. This is supported by the lack of any tendency for the chelate nitrate species to form monodentate compounds of the type $[Ni(en)_2(NO_3)H_2O]ClO_4$.

In the case of $[Ni(tet\ b)]^{2+}$, which characteristically forms triplet ground-state compounds with the tetramine in the *cis* configuration (*e.g.*, with chelates, $[Ni(tet\ b)(en)](ClO_4)_2$, or with bidentate anions, $[Ni(tet\ b)X]ClO_4$, $X = NO_3^-$, CH_3COO^-, $^1/_2C_2O_4^{2-}$,[13] BH_4^-,[15] etc.), the dinitrate occurs with one bidentate nitrate and one ionic nitrate, $[Ni(tet\ b)NO_3]NO_3$, rather than as the dinitrato compound analogous to $Ni(tet\ a)(NO_3)_2$. The same phenomenon occurs with the coordinated borohydride ion, $Ni(tet\ a)(BH_4)_2$ and $[Ni(tet\ b)BH_4]BH_4$ being formed.[15] This indicates that the electrostatic energy of interaction of the nickel(II) ion with two oxygen atoms of a nitrate ion (plus ionic lattice energy) is greater than the energy of interaction of the nickel(II) ion with an oxygen atom of two *cis* nitrate ions, minus NO_3^-–NO_3^- repulsion. With ethylenediamine, rearrangement to the *trans* arrangement can readily occur, with consequent reduction of the NO_3^-–NO_3^- repulsion, and $Ni(en)_2(NO_3)_2$ is formed.

With the nickel tetramines $[Ni(en)_2]^{2+}$, $[Ni(tet\ b)]^{2+}$, etc., $[NiN_4X]ClO_4$ compounds are formed, where X can be a variety of oxy anions, BH_4^-, etc., apparently acting as chelates. (Bis(ethylenediamine)nickel(II) chloride can be regarded as an example of a compound containing a chelating halide complex  $(en)_2Ni\genfrac{}{}{0pt}{}{\diagup Cl \searrow}{\diagdown Cl \nearrow}$.) It has been suggested that each chelate nitrate ion of $Co(R_3PO)_2(NO_3)_2$ and $[Co(NO_3)_4]^{2-}$ can be regarded as occupying one coordination position of an approximately tetrahedral complex.[1,2,4] This has been generalized to the statement that "a polyatomic ligand in which two chemically equivalent atoms are held much closer together than such a pair of atoms would be if independent of each other has a tendency to interact through both of the equivalent atoms in such a way that the mean positions of the pairs of atoms lie roughly at the vertices of one of the usual (*e.g.*, octahedral or tetrahedral) coordination polyhedra."[4] For the compounds described in this paper, and the similar substituted pyridine nickel(II) nitrate compounds described by Buffagni, Vallarino, and Quagliano,[5] it is probably more appropriate to regard the two oxygen atoms of the chelate nitrate ion as occupying two positions in a distorted octahedral arrangement. This conclusion is in agreement with the preference shown by triplet ground state nickel(II) for octahedral coordination and the rarity of five-coordinate nickel(II) compounds. The chelate nitrate ion will subtend a smaller than usual angle in the coordination sphere, but the absence of any tendency to coordinate a further group, *e.g.*, water, indicates that there is insufficient room in the coordination sphere for another donor atom.

Acknowledgment.—The financial assistance of the Research Committee of the New Zealand Universities Grants Committee is gratefully acknowledged.