871. *The Infrared and Reflectance Spectra of Some Transition-metal Nitrate and Perchlorate Dihydrates.*

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The infrared spectra of the dihydrates of manganese, cobalt, and nickel nitrates and perchlorates indicate that the anions are involved in covalent bonding to the transition-metal ions. In the perchlorates the anions are present as bidentate groups and suggest that the transition-metal ions are involved in octahedral co-ordination by two oxygen atoms from the water molecules and four from the perchlorate groups. This octahedral environment is supported by the reflectance spectra and the similarity of the spectra of the corresponding nitrates and perchlorates suggests that the nitrate ions are also involved as bidentate groups. The infrared spectrum of copper perchlorate dihydrate indicates the presence of unidentate perchlorate groups; these are interpreted as arising from the Jahn–Teller distortion of the otherwise octahedral environment of the copper ions.

The preparation of the dihydrates of manganese, cobalt, nickel, and copper dinitrates by reaction of the corresponding anhydrous metal chloride and anhydrous nitric acid has been reported,[1] as has that of the perchlorate dihydrates by dehydration of hexahydrated salts in a vacuum at ~100°.[1,2] The infrared spectra, the reflectance spectra (ultraviolet, visible, and near-infrared) and the room-temperature magnetic moments of these compounds are now reported, and a structure for the solid state is suggested.

Experimental.—Infrared spectra were determined for mulls in Nujol on a Unicam S.P. 100 spectrophotometer, the potassium bromide plates being protected by thin sheets of Polythene. Reflectance spectra were measured on a Beckman D.K. 2A recording spectrophotometer fitted with a diffuse-reflectance attachment (250—2200 mμ), the powdered samples being protected from atmospheric moisture by a quartz plate. Magnetic susceptibilities were measured at room temperature by using a Gouy balance. *X*-Ray diffraction powder patterns were obtained with a Guinier-type powder camera, and samples were sealed between two sheets of Sellotape. The samples for these physical measurements were ground and mounted in a dry-box.

Infrared Spectra.—The main infrared absorption frequencies are as tabulated. As the nitrate ion [3] has characteristic absorption frequencies at 1390, 831, and 720 cm.$^{-1}$ and the perchlorate ion [4] at 1110 and 626 cm.$^{-1}$, neither the nitrate nor the perchlorate ions are ionic in these dihydrates; they must be involved in covalent bonding to the transition

Infrared spectra of transition-metal nitrate and perchlorate dihydrates.

Nitrates, C_{2v}	ν_4	ν_1	ν_2	ν_6	ν_3	or	ν_5
Mn	1555	1310	1027	804	760		665
Co	1560—1540	1320	1055	812	760		—
Ni	1560—1540	1310	1061	810	760		—
Cu	1515	1285	1051, 1023	820, 805	770		—

Perchlorates, C_{2v}	ν_8	ν_6	ν_1	ν_2	ν_3	ν_7	ν_9	ν_4
Mn	1210	1138	1030	945	666	635, 613	467	453
Co	1208	1125	1025	935	647	628, 611	497	—
Ni	1215	1135	1035	937	645	625, 612	490	474

Perchlorate, C_{3v}	ν_4	ν_1	ν_2	ν_3	ν_5	ν_6
Cu	1158	1030	920	648	620, 605	480, 460

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[1] Hathaway and Underhill, *J.*, 1960, 648.

[2] Hathaway and Underhill, *J.*, 1961, 3091.

[3] Herzburg, " Infra-red and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co. Ltd., New York, 1945.

[4] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

metal ion through the oxygen atoms. For the nitrate ion (D_{3h}) co-ordination through one or two oxygen atoms lowers the symmetry to that of C_{2v},[5] so that it is impossible to distinguish between uni- and bi-dentate nitrate ligands. With the perchlorate ion co-ordination through one oxygen atom lowers the symmetry to that of C_{3v},[2] and co-ordination through two lowers it still further, to that of C_{2v}; and as the number of infrared active bands in the T_d, C_{3v}, and C_{2v} forms are two, six, and nine, respectively, it is possible to distinguish between these different environments of the perchlorate group by the number of infrared bands observed. For the dihydrates of manganese, cobalt, and nickel perchlorate the original ν_3 band of the perchlorate ion (1100 cm.$^{-1}$) is split into three and the normally forbidden ν_3 frequency (930 cm.$^{-1}$) appears strongly. This indicates that in these complexes the perchlorate group must act as a bidentate ligand of C_{2v} symmetry. These results do not show whether each perchlorate group is co-ordinated to one or to two metal ions and, although a bridging group is the more likely, co-ordination of two oxygen atoms of the same perchlorate ion to the same metal ion to form a four-membered ring is not impossible, especially in view of the recent evidence that the carbonate ion can do this in the complex $[Co^{III}(NH_3)_4CO_3]Cl$.[6] (Hathaway and Underhill [2] interpreted the spectrum of nickel perchlorate dihydrate incorrectly, as indicating a bidentate perchlorate group.)

The spectrum of copper perchlorate dihydrate differs from that of the first three perchlorates; the forbidden ν_1 frequency of the perchlorate ion is allowed at 920 cm.$^{-1}$, and the ν_3 band is split into two, consistent with a perchlorate group of C_{3v} symmetry. The reason for the difference in the case of copper perchlorate dihydrate probably lies in the symmetries of the d^n configuration of these transition-metal ions. If it is assumed that the lower symmetry of the perchlorate groups arises from the co-ordination of perchlorate-oxygen to the transition-metal ions and that both the water molecules present are co-ordinated to metal ions, then in the manganese, cobalt, and nickel compounds the metal ions will be six-co-ordinate (*i.e.*, octahedral) with respect to oxygen atoms, while the copper compound appears to involve only four co-ordination from two water and two perchlorate-oxygen atoms. The electron configurations of the ions is manganese(II) $d_\epsilon^3d_\gamma^2$, cobalt(II) $d_\epsilon^5d_\gamma^2$, nickel(II) $d_\epsilon^6d_\gamma^2$, and copper(II) $d_\epsilon^6d_\gamma^3$ for spin-free configurations (see below for magnetic data). In these configurations, only the copper ion will be subjected to a Jahn–Teller distortion [7] of the octahedron of oxygen atoms, usually resulting in four short bonds and two long bonds, the latter in the z-direction. Therefore, if a perchlorate-oxygen atom is co-ordinated in this z-direction the oxygen atom will be further away from, and hence more weakly bonded to, the copper ion than if bonded in the x- or y-direction. If the bond is sufficiently weak, then the symmetry of the perchlorate group may not be reduced from C_{3v} to C_{2v} and will appear to act as a unidentate ligand, in contrast to its function as a bidentate ligand in the other complexes.

Diffuse Reflectance Spectra.—The main absorption bands in the diffuse reflectance spectra of the cobalt and nickel dihydrates and the perchlorate hexahydrates are as tabulated. No spectrum was obtained for the manganese compounds because their

Diffuse reflectance spectra of the cobalt and nickel hydrates.

	NO_3^-, $n \rightarrow p$	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	${}^4T_{1g}(F) \rightarrow {}^4(A)_{2g}(F)$	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
$Co(NO_3)_2,2H_2O$	37,000	21,740sh 20,960s 20,000sh	18,180sh	8400s
$Co(ClO_4)_2,2H_2O$	—	21,740sh 20,280s 19,530s	17,090m	8580s
$Co(ClO_4)_2,6H_2O$	—	21,550sh 19,400s	16,000w	8200s
	NO_3^-, $n \rightarrow p$	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$
$Ni(NO_3)_2,2H_2O$	35,000sh	25,130s 21,280sh	15,150—13,510	8550s
$Ni(ClO_4)_2,2H_2O$		24,880s 23,260sh	14,710—12,990	7700s
$Ni(ClO_4)_2,6H_2O$		25,300s	13,500	8550s

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[5] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.
[6] Barclay and Hoskins, *J.*, 1962, 586.
[7] Orgel and Dunitz, *Nature*, 1957, **179**, 462.

$d \longrightarrow d$ transitions are very weak as they are both spin- and multiplicity-forbidden.[8] The spectra of the copper compounds were recorded, but they gave only a very broad absorption in the 14,000—10,000 cm.$^{-1}$ region without fine structure and give no precise information on the environment of the copper ion in these compounds. The bands at 36,000 cm.$^{-1}$ in the two nitrates are not charge-transfer bands but the $n \longrightarrow p$-transitions of the free nitrate ion [9] shifted to slightly higher frequencies than for the free nitrate ion in aqueous solution (33,000 cm.$^{-1}$). The spectra in the near-infrared region all show two maxima, of differing relative intensities. That of lower frequency, which occurs in all the complexes, including those of manganese and copper, at ~7000 cm.$^{-1}$ is interpreted as the first overtone of the symmetric stretching vibration of the co-ordinated water molecule.[3] The water band is most intense for the hexahydrates, as would be expected; for the dihydrates it is more intense for the perchlorates, but less intense for the nitrates, than the accompanying ligand-field band. The second maximum which always occurs on the high-frequency side of the water band is assigned as the first ligand-field band of the cobalt(II) and nickel(II) ions in octahedral co-ordination.[8] The close proximity of these two bands, combined with their differing relative intensities, has made it difficult to determine accurately the position of the first ligand-field band. Thus, while the nickel compounds indicate a sequence in the spectrochemical series [8] $H_2O,NO_3^- > ClO_4^-$, the cobalt compounds suggest the sequence $ClO_4^- > NO_3^- > H_2O$. As there is no apparent reason for this reversal it must simply be a reflection of the accuracy with which the maxima can be measured and unfortunately does not give any information on the position of the co-ordinated nitrate and perchlorate ions in the spectrochemical series. In the visible region the spectra for a given metal are very similar. For nickel there are two broad bands, one at 25,000 cm.$^{-1}$ and the other at 13,000 cm.$^{-1}$, while for cobalt a single broad band occurs at 20,000 cm.$^{-1}$. Combined with the near-infrared evidence the general appearance of these spectra is consistent with an octahedral (O_h) environment of the metal ions.[8] The cobalt(II) ion has a d^7 configuration which gives rise to a $^4T_{1g}(F)$ ground state in O_h, and transitions from this to the $^4T_{2g}(F)$ and the $^4T_{1g}(P)$ levels account for the bands at 8500 and 20,000 cm.$^{-1}$, respectively; a transition to the $^4A_{2g}(F)$ level which, as it involves a two-electron promotion, only occurs weakly and gives rise to weak absorption at 17,000 cm.$^{-1}$. The nickel(II) ion has a d^8 configuration which gives rise to a $^3A_{2g}$ ground state in O_h, and transitions form this to the $^3T_{2g}(F)$, the $^3T_{1g}(F)$, and the $^3T_{1g}(P)$ level then account for the bands at 8500, 13,500, and 25,500 cm.$^{-1}$, respectively. While these spectra are consistent with octahedral co-ordination of the metal ion, closer examination of the bands in the visible region indicates a general broadening and resolution into a number of smaller peaks in going from the hexahydrate to the dihydrates, which is especially noticeable for the cobalt compounds. For both metals the visible band concerned is a triplet level and could be split into at the most three levels by crystal fields of lower symmetry than octahedral (O_h).[8] For the dihydrates, although the metal ions are surrounded by six oxygen atoms, these are from different types of ligand, namely, two from water and four from perchlorate groups. This may be sufficient to impose a tetragonal symmetry (D_{4h}) on the transition-metal ion and split the triplet level into a singlet and a doublet level. That the ligand symmetry is not the only factor is indicated for the cobalt dihydrates, where splitting into three components has occurred; here the crystal site symmetry of the cobalt ion must be even lower than that of the first-order effect of the ligand fields. But spin–orbit coupling also contributes to this splitting. A similar result has been found with the hydrate $[Co(H_2O)_4Cl_2],2H_2O$, where the spectrum is consistent with a lower symmetry than that of D_{4h} of the six ligands surrounding the cobalt ion.[10] Without further results, for single crystals and polarised light it is impossible to

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[8] Lewis and Wilkins, " Modern Co-ordination Chemistry," Interscience Publ., Inc., New York, 1960.
[9] McConnell, *J. Chem. Phys.*, 1952, **20**, 700.
[10] Ferguson, *J. Chem. Phys.*, 1960, **32**, 533.

give a more precise description of the environment of the metal ions in these compounds. An attempt to do this is in hand.

Magnetic Susceptibilities.—The room-temperature magnetic moments of the dihydrates of manganese, cobalt and nickel are as tabulated. They indicate that the compounds are all spin-free, with magnetic moments consistent with octahedral environment of the metal ions and having significant orbital contributions to the spin-only values for cobalt and nickel, as expected in theory.[8] The magnetic moments indicate ground-state terms of $^6A_{1g}$, $^4T_{1g}$, and $^3A_{2g}$ for manganese(II), cobalt(II), and nickel(II) ions, respectively.

Room-temperature magnetic moments (μ) of the dihydrates.

Metal	Nitrates	Perchlorates	Spin-only
Manganese	6·00	5·90	5·92
Cobalt	4·73	4·73	3·88
Nickel	3·34	3·29	2·83

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