1064. *Anhydrous Cobalt(II) Nitrate and its Dinitrogen Tetroxide Adducts.*

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Anhydrous cobalt(II) nitrate forms both 1:1 and 1:2 adducts with dinitrogen tetroxide. Thermogravimetric analysis and vapour-pressure measurements on the 1:2 adduct reveal the formation of the 1:1 adduct as intermediate during thermal decomposition. Dissociation of both adducts is irreversible. Cobalt(II) nitrate is an ionic compound, but the solid adducts contain co-ordinated nitrate groups entirely. Infrared spectra support the structures $NO^+[Co(NO_3)_3]^-$ and $NO^+[Co(NO_3)_3]^-,N_2O_4$, and electrical conductivity of the 1:2 adduct in acetonitrile indicates that the ionic form exists in solution also to a small extent. Visible spectra are consistent with an essentially octahedral environment for cobalt in the simple nitrate and its adducts both in the solid state and in solution in organic solvents.

BRIEF reference has already been made to the preparation[1–4] and the infrared spectrum[2] of anhydrous cobalt(II) nitrate, to its low conductivity in nitromethane solution,[5] and to its dinitrogen tetroxide addition compound.[3,4] Recently, Dehnicke and Strähle[6] have described some properties of anhydrous cobalt(II) nitrate and its 1:1 adduct with dinitrogen tetroxide. Our results on these compounds are in general agreement with those described by Dehnicke and Strähle, and the present paper is therefore restricted to those aspects in which our results extend published information. In particular, it was observed in early work that the 1:2 dinitrogen tetroxide adduct was first formed when dinitrogen tetroxide was used as a reaction medium, whereas Dehnicke and Strähle, using either dinitrogen pentoxide or chlorine nitrate as reagents, prepared only the 1:1 compound. Both compounds do indeed exist, and their relationship to each other is discussed below. Cobalt nitrate is at present the only compound for which both 1:1 and 1:2 adducts with dinitrogen tetroxide have been isolated.

EXPERIMENTAL

1:2 Adduct.—The method used was that first employed by B. J. Hathaway in these laboratories. Metallic cobalt (5 g.) was dissolved in a mixture (100 ml.) of equal volumes of liquid dinitrogen tetroxide and ethyl acetate. The adduct crystallised from the violet liquid on addition of further dinitrogen tetroxide. The red-purple crystals were filtered off in a closed system and washed with dinitrogen tetroxide. Cobalt was determined volumetrically with e.d.t.a.; total nitrogen and dinitrogen tetroxide were determined as described previously[7] [Found: Co, 16·0; N, 23·1; N_2O_4, 50·7. Calc. for $Co(NO_3)_2,2N_2O_4$: Co, 16·1; N, 22·9; N_2O_4, 50·2%]. The compound has an appreciable vapour pressure of tetroxide at room temperature.

1:1 Adduct.—The 1:2 adduct was heated under vacuum (10^{-3} mm.) at 50°, for several hours, followed by trituration under liquid dinitrogen tetroxide. The deep pink solid was filtered in a closed system. This adduct does not evolve dinitrogen tetroxide at room temperature [Found: Co, 21·6; N, 19·5; N_2O_4, 33·2. Calc. for $Co(NO_3)_2,N_2O_4$: Co, 21·4; N, 20·4; N_2O_4, 33·5%].

It is of interest that, although cobalt(II) nitrate separates from dinitrogen tetroxide as the 1:2 adduct, the 1:1 adduct cannot be reconverted into the 1:2 by immersion in liquid dinitrogen tetroxide. The 1:1 compound appears to be identical with that prepared by Dehnicke and Strähle[6] from anhydrous cobalt(II) chloride and dinitrogen pentoxide or chlorine nitrate. The vapour pressure of the 1:2 compound is so much greater than that of the 1:1 that conversion into the latter occurs very slowly at room temperature and atmospheric pressure.

[1] A. Guntz and M. Martin, *Bull. Soc. chim. France*, 1909, **5**, 1004.
[2] C. C. Addison and B. M. Gatehouse, *J.*, 1960, 613.
[3] C. C. Addison and B. J. Hathaway, *Chem. Soc. Spec. Publ.*, No. 10, 1957.
[4] C. C. Addison, *Angew. Chem.*, 1960, **72**, 193.
[5] C. C. Addison, B. J. Hathaway, N. Logan, and A. Walker, *J.*, 1960, 4308.
[6] K. Dehnicke and J. Strähle, *Chem. Ber.*, 1964, **97**, 1502.
[7] C. C. Addison and A. Walker, *J.*, 1963, 1220.

Reaction of Dicobalt Octacarbonyl with Liquid Dinitrogen Tetroxide.—Cobalt octacarbonyl was purified by sublimation and immersed in liquid dinitrogen tetroxide at room temperature. Carbon monoxide was evolved, but the carbonyl remained insoluble in the tetroxide; a steady reaction was maintained by crushing the solid. The deep pink residue of the 1:2 adduct $Co(NO_3)_2,2N_2O_4$ was filtered off in a closed system and washed with tetroxide.

This reaction does not proceed smoothly when the reagents are diluted with light petroleum. Instantaneous reaction occurs when the two solutions are mixed, but the precipitate is not the pure 1:2 adduct. Irrespective of the concentrations used, the product invariably contained carbon (9—10%) which (from the infrared spectrum) was not present in the form of a carbonyl group. Similar products were also obtained when the reaction was carried out in methylcyclohexane. In all cases, the products exploded mildly on heating. These results suggest that an intermediate in the dicobalt octacarbonyl–dinitrogen tetroxide reaction is so reactive that it is able to attack short-chain hydrocarbons. Anhydrous cobalt(II) nitrate, liquid dinitrogen tetroxide and the adducts do not react with saturated aliphatic hydrocarbons, but tin(IV) nitrate[8] and titanium(IV) nitrate[9] do; the reactive intermediate may well be a nitrato-carbonyl in which the metal-nitrate bond is of a different type from that which exists in the pure metal nitrate.

Anhydrous cobalt(II) nitrate. The product used in these experiments was prepared by heating either adduct at 120° *in vacuo* for several hours [Found: Co, 32·1; N, 15·2. Calc. for $Co(NO_3)_2$: Co, 32·2; N, 15·3%].

Thermogravimetric Analysis.—The loss in weight of a sample over a temperature range was measured with a silica spring balance. The temperature was increased at a constant rate, and a flow of dry nitrogen through the apparatus (1 l./min) continuously removed gaseous products from the system.

Vapour Pressures.—The 1:2 adduct (0·4 g.) was heated in an evacuated vessel (118 ml.) and the pressure of the evolved gas was determined over a temperature range by means of a glass spiral gauge (sensitivity 180° deflection per atmosphere). The sample was maintained at each temperature until the change in pressure was negligible.

Electrical Conductivities.—Measurements were made over a concentration range with a conductivity cell of the type previously described.[5] In these, as in all other measurements, scrupulous precautions were taken to exclude moisture. Solvents were dried and purified by recognised procedures and samples were manipulated in a dry box.

Spectra.—Infrared spectra were determined with the Unicam S.P.200 spectrophotometer on mulls in Nujol or in Halocarbon Oil, series 11—14; windows were protected by polythene sheet as already described.[7] Reflectance spectra were measured with the Unicam S.P.500 spectrophotometer; the standard Unicam attachment was adapted for use with hygroscopic samples. Solution spectra were recorded with the S.P.500 and optically matched fused silica cells fitted with ground stoppers.

RESULTS AND DISCUSSION

Dinitrogen Tetroxide Adducts.—*Thermogravimetric analysis.* The thermal decomposition of the 1:2 adduct is shown in Fig. 1. There is clear evidence that the decomposition of the 1:2 adduct passes through the 1:1 stage, and the decomposition rate curve passes through two maxima. Even at this slow rate of heating, however, there is no actual plateau corresponding to the 1:1 compound, which is clearly of low stability in the 60—100° temperature range.

Vapour pressures. Curve A (Fig. 2) represents the variation in vapour pressure as the 1:2 adduct is heated in a closed space. The curve consists of three distinct steps. The first, up to a temperature of 35°, represents the loss of one molecule of dinitrogen tetroxide from the 1:2 adduct. The weight of the sample used was 0·403 g.; on the assumption that one only of the two molecules of dinitrogen tetroxide is lost at 35°, the calculated pressure (from the dissociation data of Verhoek and Daniels[10]) is 25·9 cm. compared with the observed value of 24—26 cm. The second stage in the range 35—70° represents a slow decomposition of the 1:1 adduct. If no decomposition of this adduct took place during this stage, the pressure

[8] C. C. Addison and W. B. Simpson, *J.*, 1965, 598.
[9] B. C. Field and C. J. Hardy, *J.*, 1963, 5278.
[10] F. H. Verhoek and F. Daniels, *J. Amer. Chem. Soc.*, 1931, **53**, 1250.

of dinitrogen tetroxide present at 35° would increase along line C. Actual pressure values, though linear with temperature, are somewhat higher. Above 70° decomposition becomes more rapid and at point P the solid will contain an appreciable amount of anhydrous cobalt(II) nitrate.
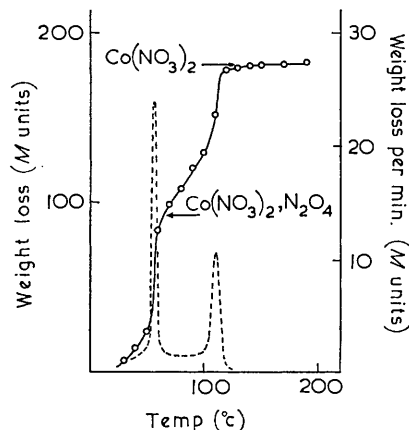

FIG. 1. Thermogravimetric analysis of $Co(NO_3)_2,2N_2O_4$ (Full line, weight loss; broken line, decomposition rates; heating rate 0·66°/min.).

The reversibility or otherwise of metal nitrate–dinitrogen tetroxide reactions is a direct reflection of the nature of the bonding between the two entities. Interaction of copper(II) nitrate with dinitrogen tetroxide is fully reversible,[11] whereas reaction with magnesium nitrate is not.[7] In studying this aspect of the chemistry of cobalt(II) nitrate, it was considered advisable to avoid isolation of the anhydrous nitrate itself, since changes in crystal structure can occur when anhydrous nitrates are heated.[12] When the system was cooled from point P, the pressure fell along the line B, the slope of which indicates that a constant quantity of dinitrogen tetroxide is present in the gas phase throughout B. Again, equilibrium pressures
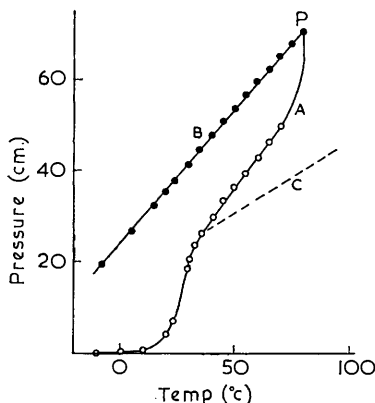

FIG. 2. Vapour-pressure changes on heating $Co(NO_3)_2,2N_2O_4$.

were established rapidly during the cooling cycle. Irreversibility was confirmed in a second experiment in which a sample of the 1:2 adduct was heated to 45°, *i.e.* to a stage at which the 1:1 adduct was only slightly decomposed. When the system was cooled from 45°, the pressure again fell linearly with temperature at a rate that indicated a constant quantity of tetroxide in the gas phase.

Previously, it has been believed that reversibility was a property of those adducts formed by nitrates of metals that readily give co-ordination complexes. In fact, the behaviour of the cobalt(II) nitrate adducts resembles most closely[7] that of $Mg(NO_3)_2,N_2O_4$.

[11] C. C. Addison and B. J. Hathaway, *J.*, 1960, 1468.
[12] N. Logan, W. B. Simpson, and S. C. Wallwork, *Proc. Chem. Soc.* 1964, 341.

Infrared spectra of adducts. The absorption bands that we have obtained for the 1:1 compound (Table 1) show some significant differences from the spectrum reported by Dehnicke and Strähle.[6] We confirm that absorption at frequencies corresponding to N_2O_4

TABLE 1.

Infrared absorption bands (cm.$^{-1}$) for cobalt nitrate–dinitrogen tetroxide adducts.

$Co(NO_3)_2, N_2O_4$			$Co(NO_3)_2, 2N_2O_4$		
2270m sp (NO^+)	1060m sp $\}$ (ν_2)		2280m sp (NO^+)	1020s (ν_2)	
1790w	1042s sp		1800m sp	805m $\}$ (ν_3)	
1730w	810m sp $\}$		1735s sp (N_2O_4)	795sh	
1590sh	805s sp $\}$ (ν_3)		1560s $\}$ (ν_1)	740s $\}$ (ν_5 and ν_6)	
1555s $\}$ (ν_1)	800m sp $\}$		1540s	730sh	
1545sh	763m sp $\}$ (ν_5 and ν_6)		1520sh		
1510sh	746m sp $\}$		1475s		
1450vs b	710m sp		1320sh		
1340sh			1290s b (ν_4)		
1280vs b (ν_4)			1245vs sp ($\nu_4 + N_2O_4$)		

vibrations are so weak as to indicate that this molecule does not exist as such in the lattice; on the other hand, Dehnicke and Strähle [6] obtained a strong band at 1365 cm.$^{-1}$, and a weak band at 835 cm.$^{-1}$, which do not occur in our spectrum. These bands are normally associated with the ν_3 and ν_2 vibrations of the free nitrate ion, and frequently arise when covalent metal nitrates are in contact with unprotected sodium chloride windows. In contrast, we find strong absorption in regions characteristic of co-ordinated nitrate groups[13] (*i.e.* in the 1040, 1280 and 1550 cm.$^{-1}$ regions), whereas Dehnicke and Strähle report only weak or negligible absorption here.

The magnetic moment (4·96 B.M.) and the reflectance spectrum (see below) of the 1:1 adduct indicate that the cobalt atom in the crystal is octahedrally co-ordinated, presumably by six oxygen atoms. The complexity of the infrared spectrum suggests that this octahedron must be considerably distorted. Cotton and Soderberg[14] have already shown that, in the complex $(Me_3PO)_2Co(NO_3)_2$, the cobalt atom is also in a highly irregular environment of six oxygen atoms. The presence of the NO^+ frequency at 2270 cm.$^{-1}$ supports the formulation[6] of the 1:1 adduct as $NO^+[Co(NO_3)_3]^-$, in which case the octahedron is provided by three bidentate nitrate groups. Symmetrical distribution of such groups around a central metal atom [as appears to be the case for tin(IV) nitrate and titanium(IV) nitrate*] gives rise to a simple infrared spectrum. Where distortion occurs, the infrared spectrum cannot be ideally assigned on either a unidentate or a bidentate basis; in Table 1 the assignments given assume bidentate bonding.[8]

The 1:2 adduct gives a spectrum that is, in general, closely similar to that of the 1:1 adduct, but sharp, strong bands due to the N_2O_4 molecule itself can now be clearly recognised. One dinitrogen tetroxide molecule is therefore present uncombined in the lattice, and the 1:2 adduct can be represented as $NO^+[Co(NO_3)_3]^-, N_2O_4$. This is entirely consistent with the behaviour of the adduct on heating.

Visible spectra. The reflectance spectrum of the 1:1 adduct consists of a broad maximum at 525 mμ and a distinct shoulder at about 485 mμ. The symmetry is therefore octahedral, but may be irregular, since a weak shoulder at about 680 mμ, is also observed. Solutions in acetonitrile give an almost identical spectrum with bands at 480sh mμ, (ε 35·3) 520 mμ (ε 44·0) and 640sh mμ, (ε 4·8). These spectra are in all respects similar to those observed for the anhydrous nitrate, which are discussed below.

Anhydrous Cobalt(II) Nitrate.—Thermal decomposition. Thermogravimetric analysis of anhydrous cobalt(II) nitrate (Fig. 3) shows that decomposition proceeds in a single step to the

* Cf. C. C. Addison, C. D. Garner, W. B. Simpson, D. Sutton, and S. C. Wallwork, *Proc. Chem. Soc.* 1964, 367.

[13] B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J.*, 1957, 4222.
[14] F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, 1963, **85**, 2402.

oxide Co_3O_4 [Weight loss found, 102 M units; required 102·7], and there is no evidence for the formation of nitrite as intermediate. Since decomposition occurs over a range of temperature, it is convenient to define decomposition temperature as that at which the decomposition rate is a maximum. Comparison with neighbouring non-volatile metal nitrates $M(NO_3)_2$ shows that the decomposition temperatures follow the sequence of atomic numbers; Mn (235°), Co (270°), Ni (300°), and Zn (350°). These values are at least 100° lower than those commonly found for the ionic nitrates of Group II. The position of the cobalt compound in this sequence is notable, since the infrared spectrum[2] supports ionic bonding in this nitrate but not in the others.
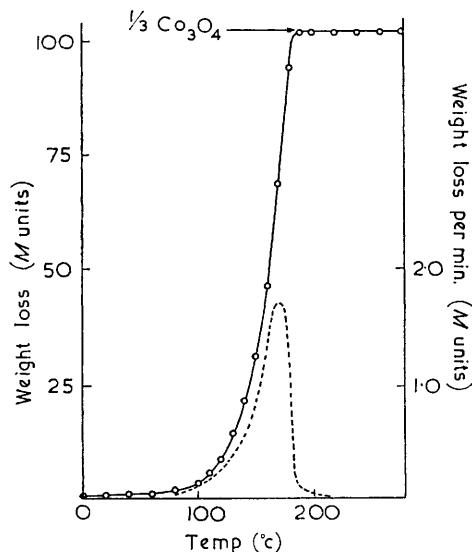

FIG. 3.   Thermogravimetric analysis of $Co(NO_3)_2$ (Full line, weight loss; broken line, decomposition rate; heating rate 0·66°/min.).

Infrared spectrum. Our measurement of the spectrum is in agreement with measurements published elsewhere,[2,6] with the exception of an additional, strong band at 1430 cm.$^{-1}$. The spectrum confirms that the compound is ionic in the solid state. A band in the 1430 cm.$^{-1}$ region occurs also in the infrared spectra of anhydrous nitrates of magnesium, calcium, strontium, and barium,[7] where it is believed that the nitrate is ionic, but of symmetry somewhat lower than D_{3h}. On combination of anhydrous cobalt(II) nitrate with dinitrogen tetroxide, the bonding of the nitrate groups therefore changes from ionic to covalent, as with magnesium nitrate.[7]

Electrical conductivities. In dimethyl sulphoxide (Fig. 4) the range of values indicates that substantial dissociation occurs; the alkaline earth nitrates show similar strong-electrolyte behaviour[15] with limiting molar conductivities also in the range 80—90 ohm^{-1}cm^2. Dr. N. Logan, in these laboratories, has shown that, in contrast to dimethyl sulphoxide (dielectric constant 46·6), nitromethane (dielectric constant 35·9) gives very weakly conducting solutions (curve D). The behaviour in nitromethane appears to be independent of the ionic or covalent nature of the nitrate itself, since very similar conductivity curves are given both by the ionic cobalt nitrate, and the covalent copper nitrate; the low conductivity in nitromethane is largely attributable to its low co-ordinating ability. The results for acetonitrile (dielectric constant 37·5) show intermediate behaviour; here the solvent competes with the nitrate for positions in the solvation shell of cobalt. The conductivity of the 1:2 adduct in this solvent (Fig. 4) is appreciably greater than that of the simple nitrate. Dinitrogen tetroxide is evolved when the adduct is dissolved in methyl cyanide; in a separate investigation,[16] however, the conductivities of solutions in dinitrogen tetroxide in methyl

[15] C. C. Addison and B. F. G. Johnson, unpublished results.
[16] C. C. Addison, C. D. Garner, and D. Sutton, unpublished results.

cyanide have been found to be only slightly greater than the very low values found for solutions of dinitrogen tetroxide in nitromethane,[17] and the difference between curves B and C (Fig. 4) cannot be accounted for by self-ionisation of the free tetroxide present in solution. The solution is best represented by the equilibrium.

$$Co(NO_3)_2,2N_2O_4 \rightleftharpoons N_2O_4 + NO^+[Co(NO_3)_3]^-$$
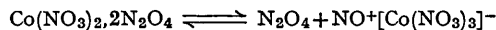
in which the ionic species is present in sufficient quantity to influence the electrical conductivity.
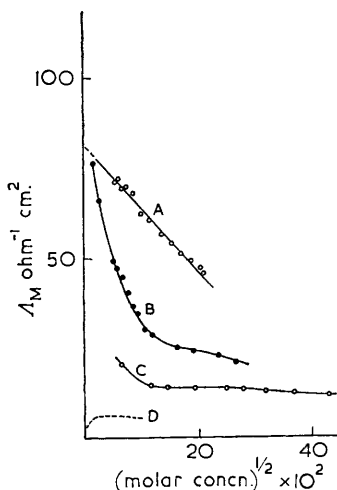
FIG. 4. Molar conductivities in non-aqueous solvents. A, $Co(NO_3)_2$ in Me_2SO; B, $Co(NO_3)_2,2N_2O_4$ in MeCN; C, $Co(NO_3)_2$ in MeCN; D, $Co(NO_3)_2$ in $MeNO_2$.

Visible spectra. The reflectance spectrum of cobalt(II) nitrate (Fig. 5) is almost identical with that of the 1:1 adduct, and indicates that the octahedron around cobalt is probably irregular in the simple nitrate also. Cobalt nitrate hexahydrate shows a very similar spectrum, but the bands are shifted to somewhat shorter wavelengths, to approximately the positions found for $[Co(H_2O)_6]^{2+}$. There is also a shoulder in the 600—700 mμ region
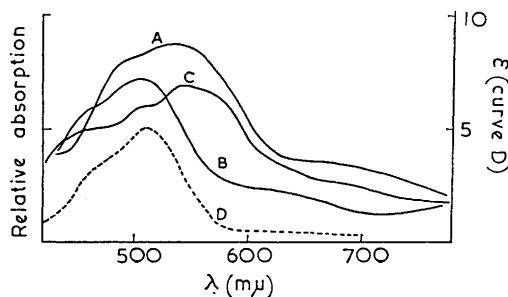
FIG. 5. Reflectance spectra. A, $Co(NO_3)_2$; B, $Co(NO_3)_2,6H_2O$; C, $CoCl_2,6H_2O$; D, $[Co(H_2O)_6]^{2+}$ by transmittance.

(curve A) which is, however, absent in curve D. Distortion is unlikely to be so severe as in the tetragonal complex *trans*-$[Co(H_2O)_4Cl_2],2H_2O$, which gives a much more complicated spectrum but does possess the 600—700 mμ shoulder.

Spectra for solutions of cobalt(II) nitrate in water and five polar organic solvents (Fig. 6.) closely resemble the reflectance spectrum. The outstanding feature here is the variation of extinction coefficient, (ε) with solvent (Table 2), which supports the conclusions drawn from the conductivity measurements.

[17] C. C. Addison, N. Hodge, and J. Lewis, *J.*, 1953, 2631.

TABLE 2.

Maximum extinction coefficients for $Co(NO_3)_2$ solutions.

Solvent.............	H_2O	Me_2SO	EtOH	EtOAc	MeCN	$MeNO_2$
$\lambda_{max.}$ (mμ)	514	542	520	537	520	520
$\varepsilon_{max.}$	5·0	11·8	25·6	42·5	45·5	78·8

In aqueous solution the ion $[Co(H_2O)_6]^{2+}$ is clearly present, and the general appearance of the spectrum for dimethyl sulphoxide solution suggests that the analogous $[Co(Me_2SO)_6]^{2+}$ ion is formed. Bands in the 600—700 mμ region are absent in both instances. For nitromethane solution, the extinction coefficient is higher than is commonly found for octahedrally co-ordinated Co^{2+} ($\varepsilon_{max.} \sim 10$), but much lower than values for tetrahedral co-ordination ($\varepsilon_{max.}$400—1700); furthermore, the bands are not greatly shifted in position.
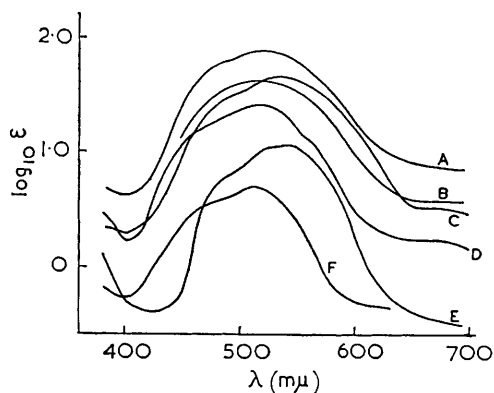

FIG. 6.   Visible spectra of $Co(NO_3)_2$ in solvents. A, $MeNO_2$; B, MeCN; C, EtOAc; D, EtOH; E, Me_2SO; F, H_2O.

There is also considerable absorption in the 600—700 mμ range. These facts point to irregular six-co-ordination such as might arise if both nitrate and solvent molecules are present in the co-ordination sphere of cobalt and the centre of inversion thereby destroyed. These results may be directly compared with the spectrum of the complex $Co(Me_3PO)_2(NO_3)_2$, which is similar and has a maximum extinction coefficient of 114 in chloroform.[18] The behaviour of cobalt(II) nitrate in other solvents is intermediate between these extremes: in particular, the results for acetonitrile support the suggestion made above that competition between nitrate and solvent is important in this medium.

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