433. *The Ultraviolet and Visible Spectra of Some Anhydrous Copper*(II) *Salts in Organic Solvents.*

By B. J. HATHAWAY and A. E. UNDERHILL.

The spectra of copper nitrate, nitrate perchlorate, perchlorate, and tetrafluoroborate in methyl cyanide and ethyl acetate are reported. The effect of adding nitrate ions (as tetraethylammonium nitrate) to solutions of copper perchlorate and tetrafluoroborate is examined and the results are discussed in terms of a concentration-dependent equilibrium $Cu^{2+} + 2NO_3^- \rightleftharpoons Cu(NO_3)^+ + NO_3^- \rightleftharpoons Cu(NO_3)_2$, with the first nitrate ion bonding much more strongly than the second.

THE visible and ultraviolet spectra of solutions of copper nitrate [1] and copper perchlorate [2] have been reported briefly. In the visible region the extinction coefficients (ε) at the absorption maximum ($\lambda_{max.}$) were shown to be the same in ethyl acetate as solvent ($\sim$51·5) but different in methyl cyanide (47·0 and 22·4, respectively). In the ultraviolet region copper perchlorate does not absorb in either solvent but copper nitrate absorbs strongly in both ($\varepsilon \sim 2000$). It has been suggested that the strong absorption of copper nitrate in this region is due to the mononitratocopper(II) cation and not to the neutral molecule of copper nitrate.[1] Support for this suggestion has now been sought from the spectra of copper nitrate perchlorate in these solvents and from spectrophotometric titrations of copper perchlorate and tetrafluoroborate with tetraethylammonium nitrate in methyl cyanide solution.

RESULTS

Absorption Spectra.—The molar extinction coefficients of copper nitrate, nitrate perchlorate, perchlorate, and tetrafluoroborate in methyl cyanide and ethyl acetate solution are given in the Table.

Extinction coefficients of some copper salts (l. mole^{-1} cm.$^{-1}$).

	Methyl cyanide		Ethyl acetate	
	750 mμ	325 mμ	820 mμ	295 mμ
$Cu(NO_3)_2$	47·0	1900	51·6	2400
$Cu(NO_3)(ClO_4)$	43·0—44·0	1260	37·4	1170
$Cu(ClO_4)_2$	22·4	0	51·4	0
$Cu(BF_4)_2$	21·8	0	23·5 *	0

* $\lambda_{max.} = 860$ mμ.

In the visible region all the extinction coefficients are low, consistent with the absorptions' arising from forbidden $d \longrightarrow d$-transitions on the copper(II) ion. In methyl cyanide solution all four salts have $\lambda_{max.}$ at 750 mμ, but copper perchlorate and tetrafluoroborate have extinction coefficients only half those of copper nitrate and nitrate perchlorate. Conductivity and

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[1] Addison, Hathaway, Logan, and Walker, *J.*, 1960, 4308.
[2] Hathaway and Underhill, *J.*, 1960, 3705.

molecular-weight measurements in this solvent have shown that the perchlorate [2] and tetrafluoroborate [3] are extensively dissociated while the nitrate is monomeric.[1] In methyl cyanide the copper ions are probably solvated by six molecules of solvent, having, we believe, a distorted octahedral structure which we ascribe to a Jahn–Teller effect.[4] In the nitrates some of these co-ordinated methyl cyanide molecules are replaced by nitrate ions and thus give rise to the observed increase in the extinction coefficients. Copper nitrate perchlorate has an extinction coefficient only slightly lower than that of the pure nitrate itself, suggesting that the species responsible for this absorption involves the association of only one nitrate ion per copper ion, *i.e.*, the mononitratocopper(II) cation is formed. This implies that in copper nitrate solution only one nitrate ion is associated sufficiently strongly to give rise to changes in the visible spectrum. But it is difficult to understand why this co-ordination, if strong enough to affect the extinction coefficient, does not change the position of the maximum.

In ethyl acetate, in the visible region, copper tetrafluoroborate differs from the other three salts in having $\lambda_{max.}$ at 860 mμ, a significantly lower extinction coefficient and a slightly higher molar conductivity (10^{-1} compared with 10^{-2} ohm^{-1} cm.^{2}) than the nitrate or perchlorate, both of which are monomeric in this solvent. The spectra of these solutions suggest that the copper ions are solvated in the equatorial plane by ethyl acetate and much more weakly co-ordinated in the *z*-direction by the anions. The copper ions in the nitrate and perchlorate would then have similar co-ordination shells, namely, four close oxygen atoms and two more distant ones, while the tetrafluoroborate would have four close oxygen atoms and two more distant fluorine atoms. This difference would then account for the shifts in $\lambda_{max.}$ in these solutions and is consistent with the relative ligand field strengths of oxygen and fluorine atoms, as predicted by Jørgensen.[5] The differences in environment of the copper ion in the nitrate and the perchlorate would not be significant as long as the two oxygen atoms attached in the *z*-direction are from the same type of anion (*i.e.*, nitrate or perchlorate). But if the two anion oxygens are from different types of anion, then, although the environment of the copper ion would be the same as in the pure nitrate and perchlorate and hence no shift in $\lambda_{max.}$ would be expected, a change in the overall symmetry of the copper ion has been introduced and a change in the intensity of the absorption would occur.[6] This type of asymmetry is introduced in ethyl acetate solutions of copper nitrate perchlorate; the extinction coefficient is lower (37·4) but at the same wavelength as for the simple nitrate or perchlorate; why there is a decrease in extinction coefficient is not understood.

In the ultraviolet region copper perchlorate and tetrafluoroborate are transparent in both methyl cyanide and ethyl acetate solution, but copper nitrate [1] and nitrate perchlorate absorb with high extinction coefficients (10^3 l. mole^{-1} cm.$^{-1}$) and at slightly different wavelengths (325 and 295 mμ, respectively). In ethyl acetate solution the extinction coefficient of the copper nitrate perchlorate is approximately half that of copper nitrate, indicating a simple relation between the extinction coefficient and the number of nitrate ions per copper ion. In methyl cyanide as solvent the absorption is due mainly to a mononitratocopper(II) species, for the extinction coefficient of copper nitrate perchlorate is here significantly greater than half that of copper nitrate. The lack of stoicheiometry indicates that this cation must be present in the following type of equilibrium:

$$\mathrm{Cu(NO_3)_2} \rightleftharpoons \mathrm{Cu(NO_3)^+} + \mathrm{NO_3^-} \rightleftharpoons \mathrm{Cu^{2+}} + \mathrm{2NO_3^+} \qquad (1)$$

$$\mathrm{Cu(NO_3)(ClO_4)} \rightleftharpoons \mathrm{Cu(NO_3)^+} + \mathrm{ClO_4^-} \rightleftharpoons \mathrm{Cu^{2+}} + \mathrm{NO_3^-} + \mathrm{ClO_4^-} \qquad (2)$$

Spectrophotometric Titrations.—In order to obtain further evidence of the equilibrium expressed in equation (1) and (2), the effect of adding nitrate ions, as tetraethylammonium nitrate, to solutions of copper perchlorate or tetrafluoroborate in methyl cyanide has been followed spectrophotometrically. Only methyl cyanide solutions could be examined in this way as tetraethylammonium nitrate is insoluble in ethyl acetate.

Fig. 1 shows the effect of added nitrate ion on the ultraviolet spectrum of copper perchlorate. As the ratio of nitrate to copper ion rises from 1 : 1 to 3 : 1 there is an increase in the extinction coefficient and a shift in the maximum to lower wavelengths. This suggests that, while the

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[3] Hathaway, Holah, and Underhill, *J.*, 1962, paper 468.

[4] Orgel and Dunitz, *Nature*, 1957, **179**, 462.

[5] Jørgensen, Report on 10th Solvay Conference in Chemistry, Brussels, 1956, p. 355.

[6] Balhausen, " Intensities of Spectral Bands in Transition Metal Complexes " in " Progress in Inorganic Chemistry," ed. Cotton, Interscience Publ., Inc., New York, Vol. II, p. 251.

mononitratocopper(II) cation absorbs at 325 mμ, the species formed by the association of further nitrate ions with this cation absorb at slightly lower wavelengths; also that the observed results are composite curves involving the addition of an approximately constant absorption at 325 mμ and an absorption at ~300 mμ which increases as the ratio of nitrate to copper increases beyond 1 : 1. This change in $\lambda_{max.}$ is reflected in the plots of observed optical density at constant copper concentration, as the ratio of added nitrate is increased, for different wavelengths (Fig. 2). At wavelengths around 335 mμ or above a maximum occurs at a 2 : 1 ratio, while at lower wavelengths no real maximum occurs, only a steady rise even up to a 3 : 1 ratio. These results, however, were found to be sensitive to the copper concentration. For 0·001M-solutions, maxima were not obtained even at the 325 mμ, suggesting that the equilibria (1) and (2) may lie to the right-hand side. Therefore not all the copper present at this concentration

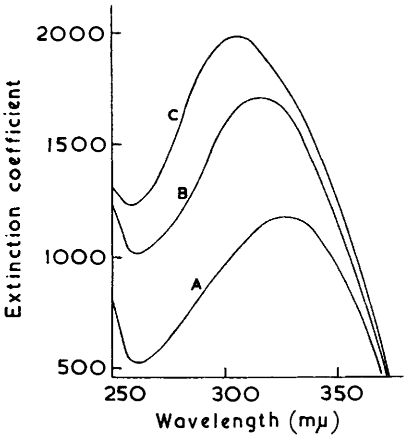

FIG. 1. Effect of added nitrate on the spectrum of copper perchlorate in methyl cyanide solution.

A, Cu : NO_3 = (A) 1 : 1, (B) 1 : 2, (C) 1 : 3.

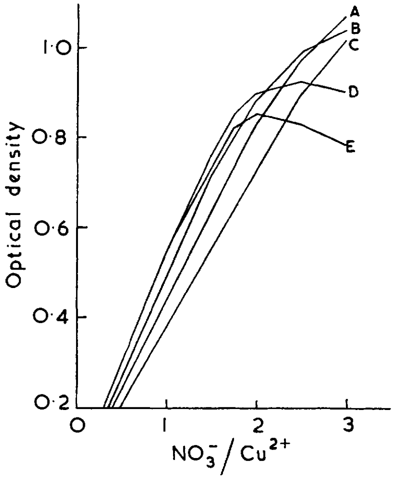

FIG. 2. Effect of added nitrate on spectrum of copper perchlorate (0·005M) at (A) 300, (B) 310, (C) 290, (D) 325, and (E) 335 mμ.

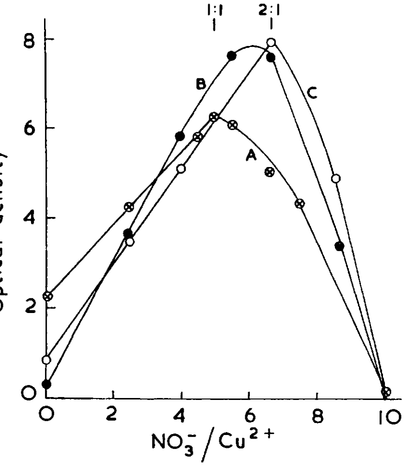

FIG. 3. Addition of nitrate to copper perchlorate in methyl cyanide: Job's method of continuous variation. A, 325 mμ, 0·001M. B, 325 mμ, 0·007M. C, 300 mμ, 0·007M.

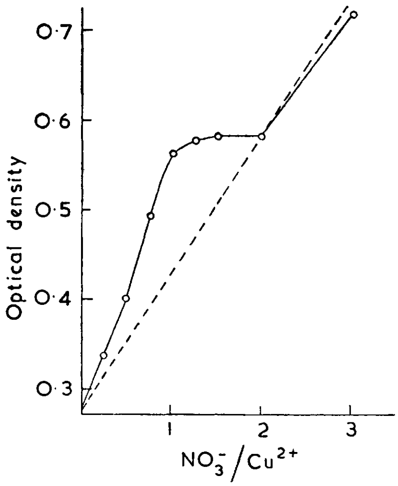

FIG. 4. Spectrophotometric titration of copper perchlorate (0·0127M) with nitrate in methyl cyanide: visible region, 750 mμ.

(0·001M) is present as the mononitratocopper(II) ion, but some free copper ions exist. Analysis of these solutions spectrophotometrically by Job's[7] method of continuous variation (Fig. 3) at low concentrations (curve A) shows a sharp maximum at a 1 : 1 composition, but at higher concentrations (curve B) a much more rounded maximum is obtained, indicating the existence of both 1 : 1 and 2 : 1 association.

The effects of adding nitrate ions to solutions of copper perchlorate on the spectra in the visible region are shown in Fig. 4. The optical density increases rapidly up to 1 : 1 stoicheiometry, but then only very slightly further to 2 : 1 stoicheiometry. The extinction coefficients at these stoicheiometries, 44·7 and 46·7, respectively, agree well with the values for copper nitrate perchlorate and nitrate (Table). The spectra in this region are not sensitive to concentration, and the same 1 : 1 association is indicated even in 0·1M-solutions, at which concentration copper nitrate is known to be monomeric. The sensitivity of the visible spectrum to the addition of only one nitrate ion per copper ion suggests that one nitrate ion is associated much more strongly than the other in the copper nitrate monomer. Therefore, copper nitrate can best be formulated as mononitratocopper(II) nitrate in which only the nitrate involved in the cation is sufficiently strongly bound to influence the spectrum in the visible region, but both nitrate groups give rise to absorption in the ultraviolet region, although at slightly different wavelengths.

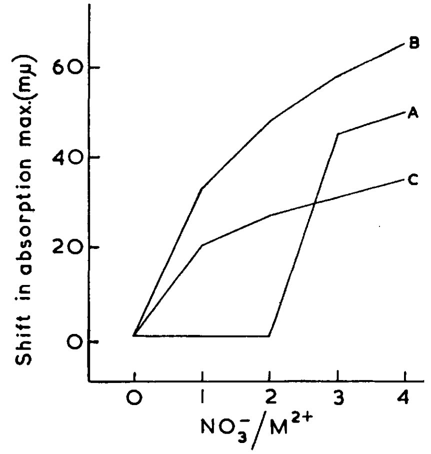

FIG. 5. Shift in $\lambda_{max.}$ on addition of nitrate ion to solutions of tetrafluoroborates in methyl cyanide (visible region): A, Copper; B, cobalt; C, nickel.

The Table shows that, although there is a change of extinction coefficient from copper perchlorate to copper nitrate perchlorate and copper nitrate, there is no change in $\lambda_{max.}$. But if further nitrate ions are added beyond the 2 : 1 ratio (of copper nitrate) a significant shift in $\lambda_{max.}$ to higher wavelengths occurs. This is shown in curve A of Fig. 5, where the shift in $\lambda_{max.}$ is plotted against the ratio of nitrate to copper ions. The effect of added nitrate ions on the visible absorption of solutions of cobalt and nickel tetrafluoroborates[3] in methyl cyanide solutions was also examined, and the results are shown as curves B and C in Fig. 5. In both cases there is a significant shift in $\lambda_{max.}$ on addition of a single nitrate ion per cation and further shifts as more nitrates are added. These results contrast with those in the case of copper.

The Origin of the Ultraviolet Absorption.—The free nitrate ion in aqueous solution has a weak absorption[1] (ε 7·01) at 302·5 mμ, which is considered to originate from an $n \rightarrow p$-transition[8] which is only weakly allowed. Katzin[9] found high ε values (~1000) in solutions of hydrated copper nitrate in t-butyl alcohol in this region and attributed them either to distortion of the electron orbitals of the nitrate ion or to distortion of the nitrate ion itself to a pyramidal form. The $n \rightarrow p$-transitions of the nitrate ion could become allowed as a result of either of these distortions, and much higher extinction coefficients would then result. While these explanations may be justified, the absorptions occur in the region where charge-transfer spectra normally appear and Stiddard[10] suggests that the high absorption of

[7] Job, *Ann. Chim.* (*France*), 1928, **9**, 113.
[8] McConnell, *J. Chem. Phys.*, 1952, **20**, 700.
[9] Katzin, *J. Chem. Phys.*, 1950, **18**, 789; *J. Inorg. Nuclear Chem.*, 1957, **4**, 187.
[10] Stiddard, unpublished work.

copper nitrate in methyl cyanide and ethyl acetate originates from charge transfer between the nitrate and the copper ions. Evidence for this [10] is the appearance of an absorption band at 260 mμ on addition of nitrate ions to copper perchlorate in aqueous solution (Hope, Otter, and Prue [11] also report a band at 255 mμ, but make no comment as to its origin). These maxima are at significantly lower wavelengths than we found, but this is consistent with their occurring in non-aqueous solutions.

Addison *et al.*[1] have suggested that the ultraviolet absorption of copper nitrate in methyl cyanide is due to the mononitratocopper(II) cation, but the above results show that this is not entirely correct. Undoubtedly this species occurs with an enhanced stability in these solutions and accounts for a significant part of the ultraviolet absorption, but the association of a second nitrate ion also contributes to the extinction coefficient in this region with a band at a slightly lower wavelength. If the origin of these absorptions is charge transfer, that from the more strongly associated nitrate ion is likely to be easier, and hence to occur at a higher wavelength, than the charge transfer from the more weakly associated nitrate ion.

The slight decrease in $\lambda_{\text{max.}}$ with increasing concentration which Addison *et al.*[1] reported for copper nitrate in methyl cyanide is consistent with dissociation in an equilibrium (1) (above). At very low concentrations the solution will contain predominantly mononitratocopper(II) cations and will have an absorption maximum at 325 mμ, while at higher concentrations copper nitrate monomer will predominate and the maximum will shift to lower wavelengths as reported.

The Origin of the Visible Absorption.—Smithson and Williams [12] have suggested that it may be possible to distinguish between complex and ion-pair formation with transition-metal ions by examination of their weak absorptions in the visible region which arise from forbidden $d \longrightarrow d$-transitions on the metal ion itself. For a number of pentamminecobalt(II) complexes with either a different ligand occupying the sixth position in the co-ordination sheath of cobalt they found significant shifts in $\lambda_{\text{max.}}$ occurred, but no shift occurred where only ion association was involved.

This criterion suggests that the two nitrate ions of monomeric copper nitrate are involved only in ion association and not in complex formation, for no shift in $\lambda_{\text{max.}}$ occurs, but that addition of a third and possibly a fourth nitrate does involve complex formation. This interpretation is difficult to understand, especially as both cobalt and nickel experience a radical shift in $\lambda_{\text{max.}}$ even on addition of one nitrate ion. With cobalt and nickel, however, both ions are involved in regular octahedral co-ordination [3] in methyl cyanide solution (cobalt $d_\epsilon{}^5\, d_\gamma{}^2$, nickel $d_\epsilon{}^6\, d_\delta{}^2$); therefore complex formation with nitrate ions must involve replacement of one of the co-ordinated methyl cyanide molecules. But as all six methyl cyanide molecules are equally co-ordinated their successive replacement will involve approximately equal shifts in $\lambda_{\text{max.}}$, as found in practice (Fig. 5). Since with copper(II) a regular octahedral co-ordination does not occur, owing to the Jahn–Teller effect,[4] the four square-coplanar methyl cyanide molecules are much more tightly bound than the two in the *z*-direction. Therefore, as the nitrate ion is only a slightly stronger ligand than methyl cyanide, it is likely that the most weakly bound molecule will be displaced first, *i.e.*, one of the two in the *z*-direction. The copper ion is still subjected to a Jahn–Teller distortion and therefore nitrate ions co-ordinated in the *z*-direction are more weakly bound than if they had replaced methyl cyanide molecules in the equatorial positions, and so they do not bring about a shift in $\lambda_{\text{max.}}$. If more than two nitrate ions become co-ordinated to a copper ion, replacement of the more strongly bound equatorial methyl cyanide molecules must take place, with a consequent shift in $\lambda_{\text{max.}}$ (Fig. 5). Thus these results are not in conflict with Smithson and Williams's suggestions, which apply to the cobalt and nickel results as the normal case: the tetragonal distortion with the copper ion makes it an exception from the general rule.

It is not understood why there should be such a large increase in extinction coefficient on addition of the first nitrate ion to solutions of copper ions, compared to that of a second. The co-ordination of one nitrate ion per copper ion will produce an element of asymmetry into the co-ordination sheath of the copper(II) ion [in the mononitratocopper(II) cation], and as the association of a second nitrate ion is much weaker this asymmetry may still be maintained in the monomer [mononitratocopper(II) nitrate]. But as our knowledge of the factors which

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[11] Hope, Otter, and Prue, *J.*, 1960, 5226.
[12] Smithson and Williams, *J.*, 1958, 457.

influence the extinction coefficient of forbidden $d \longrightarrow d$-transitions is limited [6] this explanation should be treated with caution.

The visible absorption spectrum of copper(II) ions in methyl cyanide consists of a very broad band, suggesting that it involves more than one transition. Belford, Calvin, and Belford [13] have analysed the band into three components, and Graddon [14] has suggested two components in the visible and a third in the ultraviolet region. These components can be associated with the transitions $d_{z^2} \longrightarrow d_{x^2-y^2}$, d_{xz} or $d_{yz} \longrightarrow d_{x^2-y^2}$, or $d_{xy} \longrightarrow d_{x^2-y^2}$, as the $d_{x^2-y^2}$ orbital has the highest energy for a d^9 configuration in a field of tetragonal symmetry. The first of these transitions will be the most sensitive when the ligands in the z-direction are varied, but as these are the furthest away from the copper(II) ion, owing to the tetragonal distortion, the effect will be small. Therefore, as $\lambda_{\text{max.}}$ and $\varepsilon_{\text{max.}}$ are obtained from composite experimental curves, a small variation in one of the components may not be observed in these values; but such a variation might be observed at other wavelengths. For this reason the type of analysis of Fig. 4 was extended over a wavelength range 600—1000 mμ; neverthless no significant differences were observed. These results confirm the view that, if there is any change in $\lambda_{\text{max.}}$ on addition of the first two nitrate ions, it is very much smaller than that (45 mμ) observed on addition of a third nitrate ion.

Experimental.—Anhydrous copper nitrate was prepared as described previously,[15] and copper nitrate perchlorate by reaction of copper nitrate with 2·5 mol. of nitrosyl perchlorate under a vacuum at 200°, followed by fractional sublimation. Solutions of copper perchlorate [2] and tetrafluoroborate [3] were prepared by reaction of the corresponding nitrosyl compound, in the appropriate solvent, with copper under reduced pressure. Tetraethylammonium nitrate [16] was prepared by reaction of tetraethylammonium bromide and liquid dinitrogen tetroxide, the crude product being recrystallised from methyl cyanide–ethyl acetate.

Solvents were dried and purified by standard methods and finally by distillation from copper nitrate solution.[1]

Ultraviolet and visible spectra were determined with a Unicam S.P. 100 spectrophotometer; matched fused silica cells of 1 and 10 mm. path length were used.

The authors are indebted to the Chemical Society for a grant for apparatus, and to the Department of Scientific and Industrial Research for maintenance grant (to A. E. U.).

THE UNIVERSITY, HULL. [*Received, December* 13*th*, 1961.]

[13] Belford, Calvin, and Belford, *J. Chem. Phys.*, 1957, **26**, 1165.

[14] Graddon, *J. Inorg. Nuclear Chem.*, 1960, **14**, 161.

[15] Addison and Hathaway, *J.*, 1958, 3099.

[16] Addison, Conduit, and Thompson, *J.*, 1951, 1298.