Thermochimica Acta, 23 (1978) 283–291

SPECTROPHOTOMETRIC AND THERMAL ANALYTICAL STUDIES ON THE DEHYDRATION OF COPPER(II) SULFATE AND ITS DOUBLE SALTS

K. NAGASE AND H. YOKOBAYASHI
College of General Education, Tohoku University, Kawauchi, Sendai 980 (Japan)

K. SONE
Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112 (Japan)

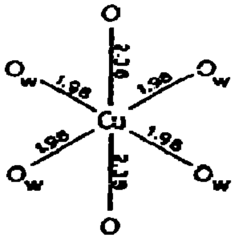
(Received 11 May 1977)

ABSTRACT

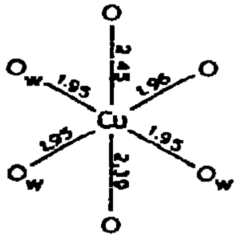
Spectrophotometric (diffuse reflection) and TG–DTA data on the dehydration of $CuSO_4 \cdot 5H_2O$, $Na_2Cu(SO_4)_2 \cdot 2H_2O$, $M_2Cu(SO_4)_2 \cdot 6H_2O$($M^+ = K^+, Rb^+, Cs^+$ and NH_4^+) and $Co_2Cu(SO_4)_3 \cdot 18H_2O$ are given. Although complete dehydration of $CuSO_4 \cdot 5H_2O$ brings about a striking color change from blue to white, it was found that there is only a slight decrease in the $\bar{\nu}_{max.}$ of its d–d band in the course of this change, and the total light absorption in the visible–UV region increases at the same time. The dehydration of the alkali metal and ammonium double salts, most of which contain $[Cu(OH_2)_6]^{2+}$ aquo ions (in contrast to the $[Cu(OH_2)_4]^{2+}$ in $CuSO_4 \cdot 5H_2O$), occurs generally more easily than that of $CuSO_4 \cdot 5H_2O$, and their $\bar{\nu}_{max.}$ increases slightly in the change, leading to blue or green anhydrous products, although the formation of a white modification was observed with the potassium salt. It was also found that the $\bar{\nu}_{max.}$ of the Cu^{2+} ion in the dehydrated cobalt(II) double salt is still lower than that in anhydrous $CuSO_4$, i.e., the ligand field and/or tetragonality around it is decreased by the presence of Co^{2+} ions.

INTRODUCTION

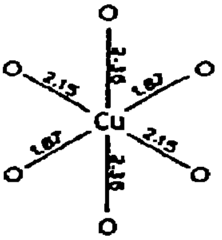
It is well known that blue $CuSO_4 \cdot 5H_2O$ loses water molecules on heating, and changes into $CuSO_4 \cdot 3H_2O$, $CuSO_4 \cdot H_2O$ and then finally white $CuSO_4$. Except for the monohydrate, the crystal structures of all these sulfates have been established by the X-ray analyses[1–3]; the coordination structure around the Cu^{2+} ions in them can be shown schematically as follows.



$CuSO_4 \cdot 5H_2O$*



$CuSO_4 \cdot 3H_2O$



$CuSO_4$

---

[*] There is another set of Cu^{2+} where the Cu–O distances are slightly longer (2.43 Å) while a pair of the Cu–O_w distances is slightly shorter (1.94 Å).

Here O_w means water oxygen and O means sulfate oxygen.

We can roughly say that they are a series of CuO_6 complexes of comparable tetragonalities, with a progressive substitution of water molecules with sulfate oxygens, although the symmetry in $CuSO_4$ is apparently lower.

Now it seems that there are no reliable data on the visible spectral changes accompanying this dehydration, although it was stated formerly by Basolo and Johnson[4] that the d–d band of $CuSO_4 \cdot 5H_2O$, which is in the red part of the visible region, must be shifted toward the IR region in the course of dehydration, owing to the decrease of ligand field strength (l.f.s.) around the Cu^{2+} ion (the l.f.s. of H_2O is stronger than that of SO_4^{2-} according to the spectrochemical series), and lead to the disappearance of the visible color. We therefore tried to get such kind of data by means of the diffuse reflectance method. We also investigated the thermal behaviors of the double salts of copper sulfate with sodium, potassium, rubidium, caesium, ammonium and cobalt sulfates by TG–DTA and reflectance spectroscopy, and tried to find some correlations between the results obtained and those on copper sulfate.

EXPERIMENTAL

Preparation of samples

Commercial copper sulfate pentahydrate (G.R. grade) was used without purification. The double salts of copper sulfate with alkali metal, ammonium and cobalt(II) sulfates were obtained generally by mixing warm solutions of the component sulfates in equivalent proportions together with a few drops of conc. H_2SO_4, and allowing the mixture to stand at room temperature. The crystals which separated out were filtrated and dried in open air. The contents of metal and H_2O in them confirmed the formulas given in Fig. 2.

Measurements

The electronic spectra of the samples before and after heating were obtained by the diffuse reflection method with a Hitachi EPS-3T spectrophotometer equipped with a standard integrating sphere attachment in the range 10000–30000 cm^{-1} at room temperature. The powder X-ray diffractograms at desired temperatures were recorded with a Toshiba ADG-101 diffractometer equipped with a Toshiba SU-021 heating cell. Cu$K\alpha$ or Fe$K\alpha$ radiations were used. The simultaneous TG and DTA were performed with a Shinku Riko TGD-3000 differential thermal microbalance in nitrogen atmosphere with a heating rate of 5°C min^{-1}. 15–20 mg of sample in a platinum crucible were used for each measurement.

RESULTS AND DISCUSSION

Copper sulfate

As shown partly in Fig. 1, the d–d band maxima of the hydrated and anhydrous copper sulfates were observed at 13200 cm^{-1} ($CuSO_4 \cdot 5H_2O$), 13000 cm^{-1} ($CuSO_4 \cdot$

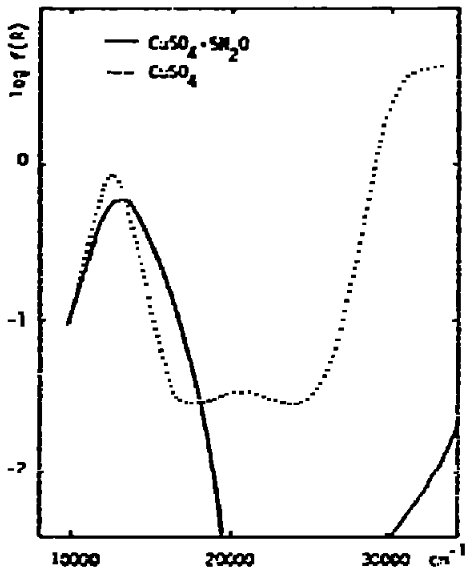


Fig. 1. Reflectance spectra of copper sulfates.

$3H_2O$), 12700 cm^{-1} ($CuSO_4 \cdot H_2O$) and 12500 cm^{-1} ($CuSO_4$), respectively, in their reflectance spectra. This is in agreement with the expectation from the spectrochemical series, and indicates that, in a series of complexes of comparable tetragonalities, the substitution of a coordinated water molecule with a sulfate oxygen weakens the apparent ligand field strength about 150–200 cm^{-1} (cf. Introduction).

In addition to this shift of the absorption maxima, the following spectral changes were observed on dehydration: (i) the width of the d–d band becomes gradually narrower with the advance of dehydration; (ii) a broad and very weak absorption appears near 20000 cm^{-1} in the spectrum of $CuSO_4 \cdot H_2O$, and, with somewhat increased intensity, in that of $CuSO_4$; and (iii) a strong absorption (probably a charge-transfer band) appears in the ultraviolet, and shifts remarkably to the lower frequency side with the advance of dehydration, indicating that the SO_4^{2-} ions are getting more and more strongly bonded, as more and more sulfate oxygens are getting coordinated in the *x*–*y* plane of the complex and shared among many Cu^{2+} ions. The nature of the weak band near 20000 cm^{-1} is uncertain, but this band may be due to a highly square planar species formed in a small quantity, since it is known[5] that such a copper(II) complex with a substituted acetylacetonate ligand gives characteristic bands in the region 15000–20000 cm^{-1}.

Both the slight red shift and narrowing of the d–d band contribute to the disappearance of the blue color in going from $CuSO_4 \cdot 5H_2O$ to $CuSO_4$, but it is interesting to note that the total light absorption in the visible-UV region increases remarkably in the same change.

The infrared spectra of the copper sulfates are expected to give further information on the binding states of SO_4^{2-} and H_2O in them. In the case of the pentahydrate, the triply degenerate stretching vibrations (ν_3) and the totally symmetric stretching vibration (ν_1) of SO_4^{2-} were observed around 1100 cm^{-1} and at 980 cm^{-1}, respec-

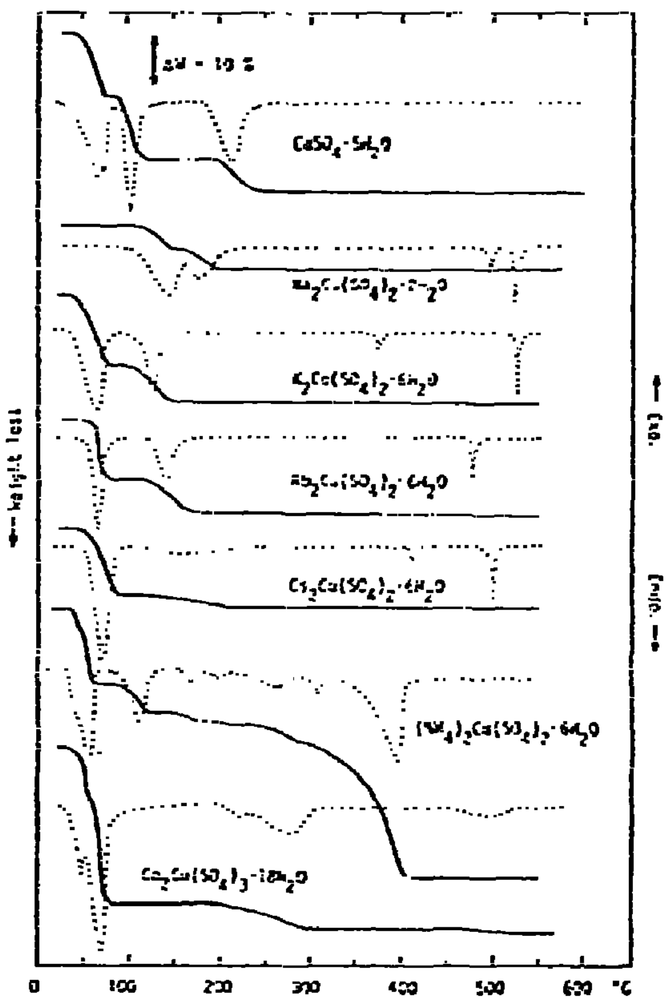


Fig. 2. TG (solid line) and DTA (dotted line) of copper sulfate and its double salts in nitrogen.

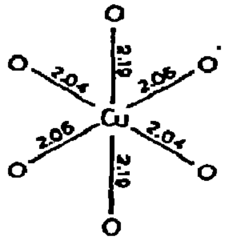
tively, the latter with a very weak intensity. As for the trihydrate, ν_3 appeared at 1070 and 1130 cm^{-1}, but ν_1 was scarcely observable. At the stage of the monohydrate, a large splitting of ν_3 (1065, 1100 and 1196 cm^{-1}) was observed and ν_1 with a medium intensity appeared at 1018 cm^{-1}. ν_3 of anhydrous copper sulfate appeared at 1079, 1090(sh), 1150, and 1210(sh)cm^{-1}, and its ν_1 appeared at 960 cm^{-1} with a strong intensity. These data show that stronger coordination of SO_4^{2-} is accompanied by a remarkable lowering of its symmetry, especially in the latter two salts[6]. The rocking mode of H_2O in the pentahydrate (ca. 870 cm^{-1}) also splits into two in the trihydrate and monohydrate (68 and 63 cm^{-1}, respectively), seemingly indicating that hydrogen bondings in them are considerably stronger than those in the pentahydrate.

Double salts of copper sulfate

It is now of interest to compare the data on copper sulfate with those on some double sulfates of copper. Figure 2 shows the TG–DTA curves of the sulfates studied. As an example, the data on $K_2Cu(SO_4)_2 \cdot 6H_2O$ will be considered in some detail. This salt is dehydrated in two steps ($-4H_2O$ at 43–73 °C and $-2H_2O$ at 93–146 °C, i.e., much more easily than $CuSO_4 \cdot 5H_2O$), and the anhydrous salt shows two endotherms at 370 °C and 520 °C (m.p.) without any weight loss.

The d–d band maximum shifts from 12800 cm^{-1} (hexahydrate) to 13000 cm^{-1} (dihydrate) and next to 13200 cm^{-1} (anhydrous salt) in the course of dehydration. The direction of this shift is thus apparently opposite to that observed with copper sulfate.

Now the crystal of the hexahydrate is known to be isomorphous with that of the ammonium salt, in which discrete $[Cu(OH_2)_6]^{2+}$ ions with the following bond lengths exist[7]:

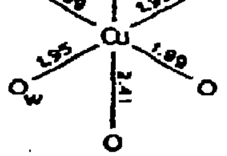


$(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$

It is clear that the tetragonality of this CuO_6 complex is much lower (i.e., it is much more octahedral) than that of the complex in $CuSO_4 \cdot 5H_2O$, which can be expressed as a planar $[Cu(OH_2)_4]^{2+}$ ion with two weakly bonded anions above and below. This is probably the reason why the $\tilde{\nu}_{max.}$ value of this double salt is lower than that in $CuSO_4 \cdot 5H_2O$ since, among Cu(II) complexes with similar ligands, the decrease of tetragonality often tends to lower the $\tilde{\nu}_{max.}$. On the other hand, the structure of the anhydrous double salt still seems to be unknown. However, we can imagine that here the sulfate ions can be coordinated much more effectively, with higher l.f.s. or increased $\tilde{\nu}_{max.}$, than in anhydrous copper sulfate. This is because a sulfate ion in anhydrous copper sulfate must form six copper–sulfate bonds altogether, while that in the anhydrous double sulfate must form only three, if a Cu^{2+} ion in it is six-coordinate as well. And, since there are two sulfate ions for a copper ion in the double salt, they may arrange themselves around the copper ions in a more favorable way (possibly forming a more tetragonal structure) than in anhydrous copper sulfate, raising the $\tilde{\nu}_{max.}$ still more. These are probably the reasons why the $\tilde{\nu}_{max.}$ value of the anhydrous double salt is higher than that of anhydrous copper sulfate*.

---

* The following bond lengths in $Na_2Cu(SO_4)_2 \cdot 2H_2O$, of which the structure has been made clear by the X-ray analysis[8], indicate that such an increase in tetragonality also occurs in the course of the hexahydrate → dihydrate change (the bond lengths in $K_2Cu(SO_4)_2 \cdot 2H_2O$ still seem to be unknown, but the X-ray diffractograms of both the dihydrates are similar, suggesting that they are isomorphous).



$Na_2Cu(SO_4)_2 \cdot 2H_2O$

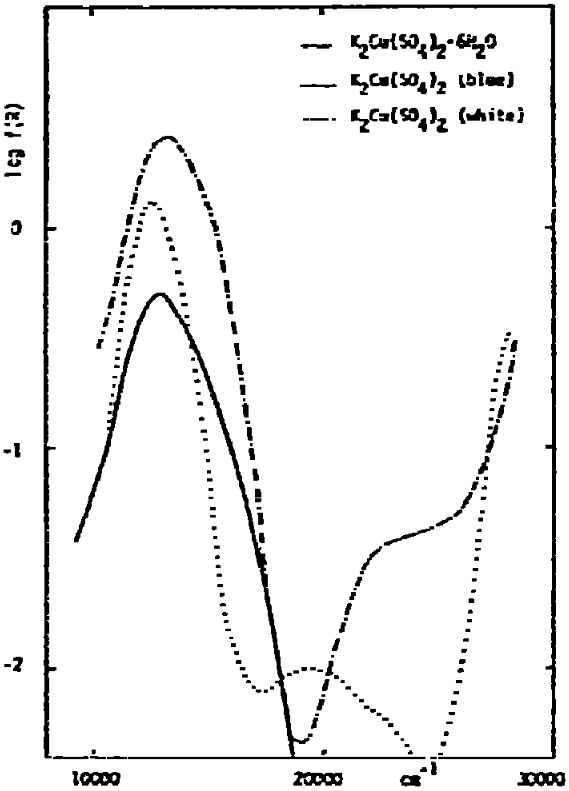


Fig. 3. Reflectance spectra of potassium copper sulfates.

All these effects may explain why the $\bar{\nu}_{max.}$ of the double salt increases with dehydration, in contrast to the case of the hydrated copper sulfate where the spectral shift occurs in the opposite way.

The anhydrous double salt thus obtained was blue and of poor crystallinity, but it is interesting to note that, as was pointed out by Pickering[9], it changes into a white crystalline modification at 190–200°C, although the complete conversion was achieved only when it was kept above 190°C for several hours. The reflectance spectra of the blue and white salts are shown in Fig. 3, together with that of the original hexahydrate. The d–d band maximum of the white one (12500 cm^{-1}), and also its spectral pattern, were very similar to those of the anhydrous $CuSO_4$, indicating their structural resemblance. On the other hand, the blue one shows a characteristic band of unknown origin* at 23800 cm^{-1}, overlapping with the charge transfer band.

As to the other double salts in Fig. 2, the following results were found: $Na_2Cu(SO_4)_2 \cdot 2H_2O$ ($\bar{\nu}_{max.}$ = 12900 cm^{-1}) loses one water at 115–149°C and one more at 149–205°C, and the blue anhydrous salt ($\bar{\nu}_{max.}$ = 13000 cm^{-1}) gives two endotherms at 499°C and 525°C (m.p.). $Rb_2Cu(SO_4)_2 \cdot 6H_2O$ ($\bar{\nu}_{max.}$ = 12800 cm^{-1}) loses $4H_2O$ at 56–73°C to form the dihydrate ($\bar{\nu}_{max.}$ = 13000 cm^{-1}) and then loses $2H_2O$ at 117–166°C. The blue anhydrous salt ($\bar{\nu}_{max.}$ = 13000 cm^{-1}) changes gradually to

---

* It was suspected that this may be due to the existence of dimeric units (such as those in copper(II) acetate), but magnetic susceptibility measurements could not prove this.

deep green on further heating and melts at 475°C. $Cs_2Cu(SO_4)_2 \cdot 6H_2O$ ($\bar{\nu}_{max.}$ = 12700 cm^{-1}) loses most of its water molecules at 46–82°C and the rest (0.7 H_2O) at 116–230°C to form yellowish green anhydrous salt ($\bar{\nu}_{max.}$ = 12800 cm^{-1}) which shows two endotherms at 413°C and 499°C (m.p.). These double salts differs from the potassium salt in two points, i.e., they are quite well crystalline even just after dehydration, and they are colored in blue or green over all the temperature range studied.

For all the double salts, it can be seen that: (i) the double salts are dehydrated more easily than $CuSO_4 \cdot 5H_2O$*; and (ii) $\bar{\nu}_{max.}$ of the d–d bands tends to increase on dehydration, possibly owing to the destruction of the $[Cu(OH_2)_6]^{2+}$ unit and formation of the more tetragonal structures with SO_4^{2-} ions of enhanced coordination ability. Infrared measurements give an additional support to this assumption, because the ν_3 of the anhydrous double salts are split into a large number of peaks distributed over a much wider frequency range than in the case of the anhydrous copper sulfate, pointing to a very low symmetry of the SO_4^{2-} ions and indicating that widely different sorts of strong and weak bonds between Cu(II) and sulfate oxygens exist in the anhydrous double salts. The spectrum of $Na_2Cu(SO_4)_2$ is shown in Fig. 4, as an example, together with that of $CuSO_4$.

It may be added that: (iii) the double salts melt far below the melting points of the constituent alkali metal sulfates; and (iv) except for the Rb salt which shows a

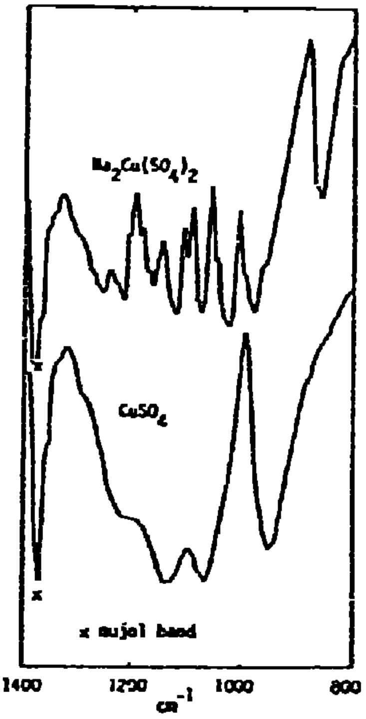


Fig. 4. Infrared spectra of $Na_2Cu(SO_4)_2$ and $CuSO_4$ in S–O stretching region.

---

* This may be attributed, at least in part, to the enhanced coordination ability of SO_4^{2-} in the double salts.

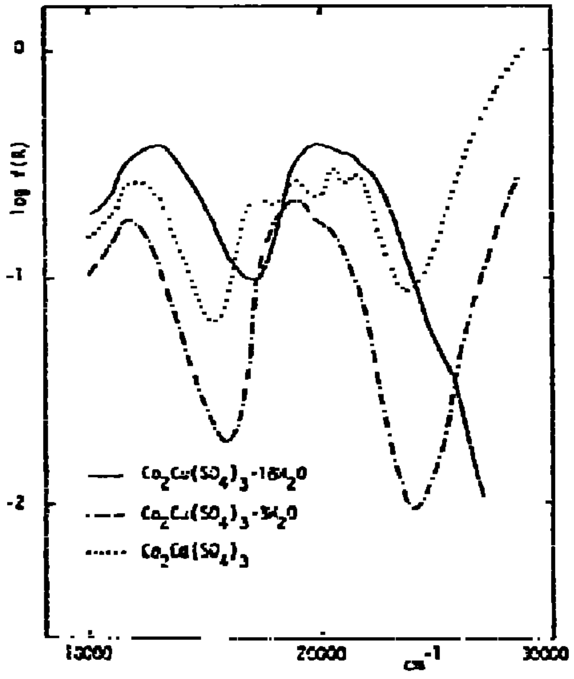


Fig. 5. Reflectance spectra of cobalt copper sulfates.

continuous (and reversible) color change to green by heating, they show a reversible thermochromism through the endothermal passage observed before melting, especially when the anhydrous salts are heated in vacuum capillaries. The white $K_2Cu(SO_4)_2$ in such a capillary changes reversibly into a green modification at 370°C, while the Na and Cs double salts change generally from greenish blue or yellowish green to deep green at 499 and 413°C, respectively.

Double salts of copper sulfate with colored heavy-metal sulfates are also interesting objects for study. As an example of them, the dark pink cobalt salt $Co_2Cu(SO_4)_3 \cdot 18H_2O$ ($\bar{\nu}_{max.} = 13200$ cm^{-1}) was studied. This salt loses $15H_2O$ in the range 32–76°C, forming pink trihydrate ($\bar{\nu}_{max.} = 12100$ cm^{-1}), which is very stable against heating but loses $3H_2O$ in the wide range 200–300°C to form violet anhydrous salt ($\bar{\nu}_{max.} = 11800$ cm^{-1}). The d–d bands due to Co^{2+} ions are also observed in the spectra of these salts, and the general spectral patterns shown in Fig. 5 can be considered, approximately, to be the superpositions of the spectra of their constituent salts ($CoSO_4 \cdot 6H_2O + CuSO_4 \cdot 5H_2O$, $CoSO_4 \cdot H_2O + CuSO_4 \cdot H_2O$, and $CoSO_4 + CuSO_4$), although the d–d band maxima of the Cu^{2+} ions in the trihydrate and anhydrous salt appear at the lower frequency side, compared with those of the corresponding copper sulfates. This may be taken as an indication that the apparent l.f.s. of SO_4^{2-} ions around a Cu^{2+} ion is weakened, and/or their tetragonality is lowered, when they are shared with Co^{2+} ions.

The present work thus shows that the thermal properties of double salts, and the spectral changes accompanying them, can sometimes be quite different from those of the constituent salts. It is expected that further investigations on other types of double salts will bring about interesting new information in this field of inorganic thermochemistry.

ACKNOWLEDGEMENT

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education (Japan).

REFERENCES

1 G. E. Bacon and N. A. Curry, *Proc. Roy. Soc.*, 266A (1962) 95.
2 R. Zahrobsky and W. H. Baur, *Naturwiss.*, 52 (1965) 389.
3 P. A. Kokkoros and P. J. Rentzeperis, *Acta Crystallogr.*, (1958) 361.
4 F. Basolo and R. C. Johnson, *Coordination Chemistry*, Benjamin, New York, 1964, p. 86.
5 F. A. Cotton and J. J. Wise, *Inorg. Chem.*, 6 (1967) 917.
6 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 1970, p. 173.
7 M. W. Webb, N. F. Kay and N. W. Grimes, *Acta Crystallogr.*, 18 (1965) 740.
8 B. R. Rao, *Acta Crystallogr.*, 14 (1961) 738.
9 J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 3, Longmans, London, 1923, p. 258.