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STRUCTURAL AND THERMAL STUDIES ON THE ION-PAIRS $[Co(NH_3)_6]_5[HV_{10}O_{28}]_3 \cdot 18H_2O$ AND $[Co(NH_3)_6][V_2O_6OH]$

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Abstract

Two cobalt hexammine-vanadate ion-pair complexes have been prepared; one in acid medium (pH≈4) and the other in alkaline medium (pH≈10). The formed complexes were characterized by their elemental analysis, IR and XRD techniques. The complexes were subjected to thermogravimetric and differential thermal analyses. The IR study suggests that the formed complexes were of the ion-pair type, while that of the thermally decomposed compounds revealed the resolution of the originally present broad V=O and V–O–V bands.

Keywords: cobalt, hexammine-vanadate, ion-pair complexes

Introduction

Little work has been described in literatures concerning vanadates of transition metal complexes and very few of such ion-pairs have been characterized [1, 2]. Physical methods, including Raman spectra, proved that various vanadate species are formed at different pH values. At high pH values dinuclear and trinuclear species are formed; for example at pH≈10; $[V_2O_6OH]^{3-}$ and $[V_3O_9]^{3-}$ species are produced depending on the concentration of vanadium in solution. As the basicity is reduced; polyanions such as $[HV_{10}O_{28}]^{5-}$ and $[H_2V_{10}O_{28}]^{4-}$ are formed at low pH values [3, 4].

The thermodynamics of some outer-sphere molybdate and tungstate complexes of some cobalt ammoniates have also been studied [5, 6]. For supported vanadium pentaoxide, a number of attempts have been undertaken to study the structure of loaded vanadium species [7, 8]. It was suggested that V=O bond is strongly affected by the presence of the support [9].

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Experimental

Materials and methods

All reagents used in the present study were of AR or extra pure grades. The simple complex $[Co(NH_3)_6]Cl_3$ was prepared by the method described in literature [10].

Ammonium metavanadate solution

pH value of 0.05 M solution of ammonium metavanadate, used in the preparation of the ion-pairs under study, was adjusted once by dilute acetic acid to pH≈4 and another by dilute ammonia solution to pH≈10.

Preparation of the ion pairs

The vanadate solution of the proper pH was added dropwise with constant stirring to 50 ml of 0.02 M solution of the hexammine cobalt(III) chloride solution of the same pH value, where brown and orange-red crystals were obtained at pH values 4 and 10, respectively. This process was continued until complete precipitation. The precipitate was digested on a water bath for 3 h, filtered, washed several times with distilled water, ethanol and finally with ether. The crystals obtained were kept in a desiccator over silica gel. The solubility of the obtained ion-pairs were extremely low.

Regarding the solution of pH≈4, complete precipitation of the brown crystals took place when the ratio of Co:V was 1 to 6. Elemental analyses of the formed ion pair were

	%H	%N	%Co	%V
Found	3.34	11.39	8.10	41.70
Calculated	3.22	11.42	8.00	42.00

which suit the formula: $[Co(NH_3)_6]_5[HV_{10}O_{28}]_3 \cdot 18H_2O$.

At pH≈10, complete precipitation of the orange crystals took place when the ratio of Co:V was ≈1 to 2. The elemental analyses of the formed ion-pair were

	%H	%N	%Co	%V
Found	5.11	22.29	15.67	27.22
Calculated	5.05	22.34	15.69	27.13

which suit the formula: $[Co(NH_3)_6]_5[V_2O_6OH]$.

Techniques

The following techniques and measurements were carried out on the prepared ion-pairs. i) Elemental analyses, for H and N, were carried out at the microchemical analysis center, Ain Shams University. ii) The IR and FTIR spectra were recorded on a Perkin Elmer spectrometer over the range 400 to 4000 cm^{-1}, using the KBr disc technique. iii) Thermogravimetric (TG) and differential thermal analyses (DTA) were obtained using Stanton Red Croft STA-78, simultaneous thermal analyser (rate 5°C min^{-1}, 50 mL min^{-1} N_2 at atmospheric pressure).

The X-ray diffraction pattern were made on a Philips diffractometer unit Model PM 9920/03 using Cu filter – Ni radiation. The *d*-distances were calculated and their relative intensities compared with data from the ASTM cards [11, 12].

Cobalt and vanadium contents of the complexes prepared were determined volumetrically with EDTA after destruction of the complexes with nitric acid [13]. The results were confirmed by atomic absorption measurements.

Results and discussion

The ion-pair formed at pH≈4

Thermal and structural characteristics

Thermogravimetric analysis of the simple cobalt ammine complex $[Co(NH_3)_6]Cl_3$ over the temperature range ambient – 700°C has been described before [14]. The thermogravimetric treatment of the formed ion-pair complex $[Co(NH_3)_6]_5[HV_{10}O_{28}]_3\cdot 18H_2O$ is characterized by three main decomposition steps as shown in Fig. 1a and Table 1. The first step commences above 50°C showing a slow decomposition stage up to 205°C which is accompanied by ~8.1% mass loss. This loss fits well with the evolution of 18 water molecules according to the following equation:

$$[Co(NH_3)_6]_5[HV_{10}O_{28}]_3\cdot 18H_2O \rightarrow [Co(NH_3)_6]_5[HV_{10}O_{28}]_3 + 18H_2O$$

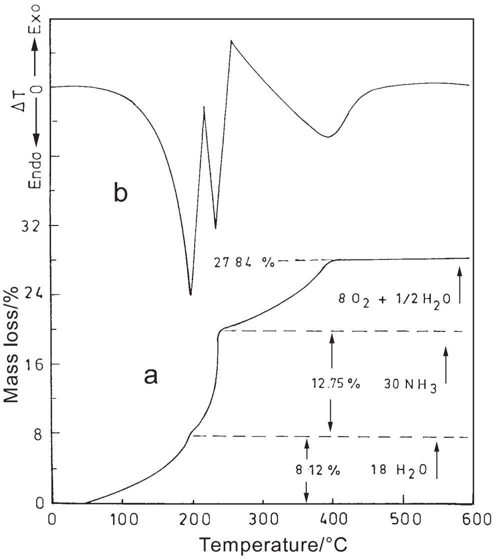

Fig. 1 Thermogravimetric (a) and differential thermal analysis (b) curves for $[Co(NH_3)_6]_5[HV_{10}O_{28}]_3\cdot 18H_2O$

Table 1 The percentage losses and corresponding detached species encountered upon heating the formed ion-pairs

Step	Temperature/ °C	Species abstracted from solid	Experimental loss/%	Theoretical loss/%
		a) $[Co(NH_3)_6]_5[HV_{10}O_{28}]_3 \cdot 18H_2O$		
First	205	$-18H_2O$	8.12	8.09
Second	240	$-30NH_3$	12.75	12.7
Third	400	$8O_2+1/2H_2O$	6.97	6.9
		b) $[CO(NH_3)_6][V_2O_6OH]$		
First	260	$-6NH_3$	27.21	27.13
Second	310	$-1/2H_2O$	2.42	2.39

The second decomposition step follows immediately after the first one terminates at ~240°C. In this step a value of 12.74% mass loss is further obtained that fits well with the evolution of 30 ammonia molecules. This is represented by the following equation:

$$[Co(NH_3)_6]_5[HV_{10}O_{28}]_3 \rightarrow Co_5[HV_{10}O_{28}]_3+30NH_3$$

The absence of ammonia in the solid product was confirmed by testing the remaining material of a sample, heated to this temperature, with hot concentrated sodium hydroxide solution, and also by the disappearance of the IR characteristic bands of ammonia as shown in (Fig. 2c). The third decomposition step (240–400°C) is characterised by a slow decomposition stage accompanied by a 6.97% mass loss and resulting in the mixed oxides, CoO, V_2O_5 and VO_2, with the reduction of Co(III) [15] and the partial reduction of V(V); a phenomenon which has been previously explained as being due to the formation of a nonstoichiometric vanadium oxide [16].

The results of differential thermal analysis reproduce the same previous speculation as shown in Fig. 1b. Two endothermic peaks are observed centering at 205 and 240°C, which correspond to two major decomposition stages. In case of the first endotherm, the peak covers the first decomposition step observed in TG as a result of the evolution of the 18 water molecules, whereas the second one reflects the evolution of the 30 ammonia molecules. After the second decomposition step an exothermic peak centered at 255°C appears immediately which may be due to change in crystal modification, and also another weak endothermic peak centered at 400°C due to another crystal modification of mixed vanadium oxides of lower valence. The existence of more than one phase of vanadium oxides above 400°C was reported in a previous investigation [16]. The reduction of Co(III) to Co(II), probably place in an early stage of the decomposition similar to other systems in which a change of valency to lower oxidation states was observed [15, 17].

IR study

The vibrational spectra of cobalt(III) hexammine chloride has been extensively studied and reviewed by Schmidt and Müller [18]. Infrared spectral analyses, obtained

Table 2 The percentage losses and corresponding detached species encountered upon heating the formed ion-pairs

Compound	$\gamma_a NH_3$	$\gamma_s NH_3$	$\delta_d NH_3$	$\delta_s HNH$	$P_r NH_3$	ν(Co–N)	ν(V=O)	ν(V–O–V)
$[Co(NH_3)_6]Cl_3$	3240	3160	1619	1329	831	498		
V=O							(1050–800)	
Vanadium oxides								770, 565, 589, 480
$[Co(NH_3)_6]_5[HV_{10}O_{28}]_3 \cdot 18H_2O$	3285	3177	1638	1333	828	495	917	751, 609, 565, 480
$[Co(NH_3)_6][V_2O_6OH]$	3285	3177	1616	1356	828	490	902, 805	705, 505, 480

before and after heating the formed ion-pair, has been studied Fig. 2a and Table 2 and showed that the formed ion-pair is characterized by the antisymmetric and symmetric NH_3 stretchings, the NH_3 degenerate deformation, the NH_3 symmetric deformation, and the NH_3 rocking vibrations appearing at 3285, 3177, 1638, 1333 and 828 cm^{-1}, respectively, in addition to the Co–N band near 500 cm^{-1}. Also, the strong band at 917 cm^{-1} due to V=O stretching vibration and the bands at 751, 601 and 480 cm^{-1} due to the O–V stretching frequencies, were observed. These bands are formed when the condensation of vanadate ions takes place in acid medium forming the $[HV_{10}O_{28}]^{5-}$ anion [19, 20]. The bands at 3566 and 1400 cm^{-1} are ascribed to combined water. It is noticed that all the shifts in the IR bands of the cationic cobalt hexammine complex and of V=O and V–O–V bands are relatively small, as shown in Table 2, confirming the assumption that the formed compound is of ion-pair type, where no appreciable

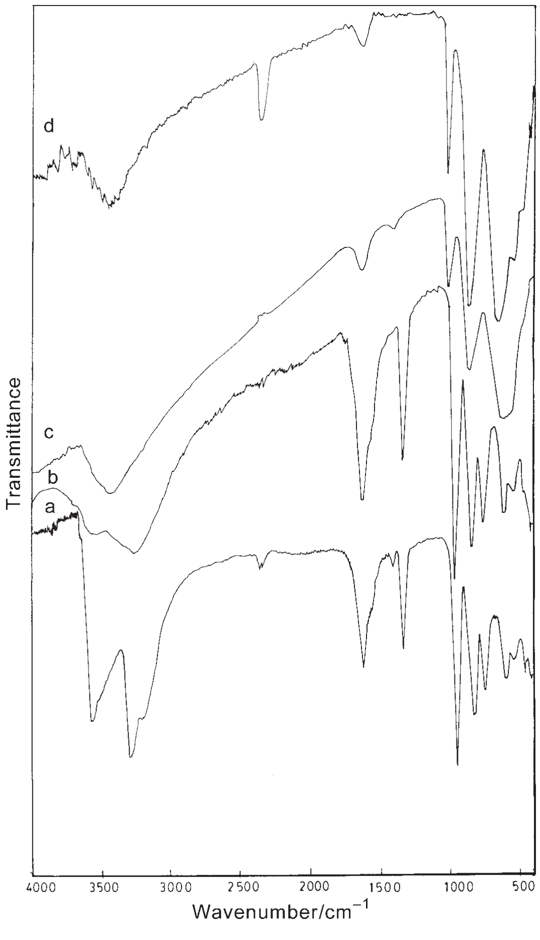

Fig. 2 Infrared spectra of a – $[Co(NH_3)_6]_5[HV_{10}O_{28}]_3\cdot18H_2O$ ion-pair; b – the ion-pair heated at 205°C; c – the ion-pair heated at 250°C; d – ion-pair heated at 500°C

change in bonding inside the cation or the anion takes place. This was previously observed by Coomber and Griffith [21]. The infrared spectral analyses obtained after heating the ion-pair complex at 205°C for 1 h showed that the four vibrational bands of NH_3 still exist (Fig. 2b). These bands disappear on heating to 250°C for 1 h confirming the complete loss of ammonia drawn from the TG study (Fig. 2c). On heating to 500°C for one h, the V=O and V–O–V bands suffered from a shift from 902, 805 to 1020 and 866 cm^{-1} and from 565 to 558, respectively as shown in Fig. 2d. The band at 662 cm^{-1} is assigned to Co(II)–O and the bands at 480 and 465 cm^{-1} to the newly formed lower oxidation state of vanadium [22].

X-ray analysis

Figure 3a represents the XRD lines of the hydrated ion-pair formed at pH≈4 which are characterized by new, very strong, diffraction lines at *d*=3.19, 3.07, 3.02, 2.71, 2.31, 1.75 and 1.515 Å; these lines are in addition to that of the original ion [11]. And that of the sample heated to 500°C, as shown in Fig. 3b, shows characteristic diffraction lines at *d*=4.7, 4.25, 3.37 and 2.76 Å due to lower vanadium oxides and also the specific diffraction lines at *d*=2.469, 2.17 and 1.932 Å due to CoO.

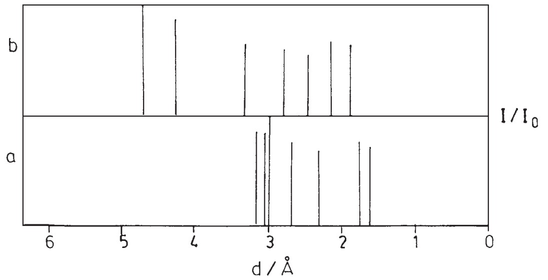

Fig. 3 XRD lines of a – $[Co(NH_3)_6]_5[HV_{10}O_{28}]_3\cdot 18H_2O$ ion-pair; b – the ion-pair heated at 500°C

The ion-pair formed at pH≈10

Thermal and structural characteristics

The thermogravimetric analysis of the ion-pair over the temperature range ambient –750°C is characterized by two main decomposition steps shown in Fig. 4a and Table 1b. The first step takes place between 200 and 260°C accompanied by a 27.21% mass loss according the following equation:

$$[Co(NH_3)_6][V_2O_6(OH)] \rightarrow Co[V_2O_6(OH)]+6NH_3\uparrow$$

The absence of ammonia in the product was confirmed by testing with hot concentrated sodium hydroxide and elemental analysis as well as by IR analysis.

The second decomposition step follows immediately the first one and termines at ≈310°C giving a total mass loss of 29.63%. In this step the obtained loss fits well with the following postulated decomposition processes:

$$2Co[V_2O_6(OH)] \rightarrow Co_2O_3+2V_2O_5+H_2O.$$

DTA results (Fig. 4b) are in accordance with the same previous speculations; thus, two main endothermic peaks are observed centering at 260 and 310°C corresponding to the two TG decomposition stages. A small endothermic peak centered at 400°C without any mass loss observed which may represent the crystal modification of V_2O_5. Another small endothermic peak at 730°C, due to its melting, is noted which is higher than that of pure V_2O_5. This strongly suggests that the presence of cobalt(III) oxide retards the melting of V_2O_5 [9].

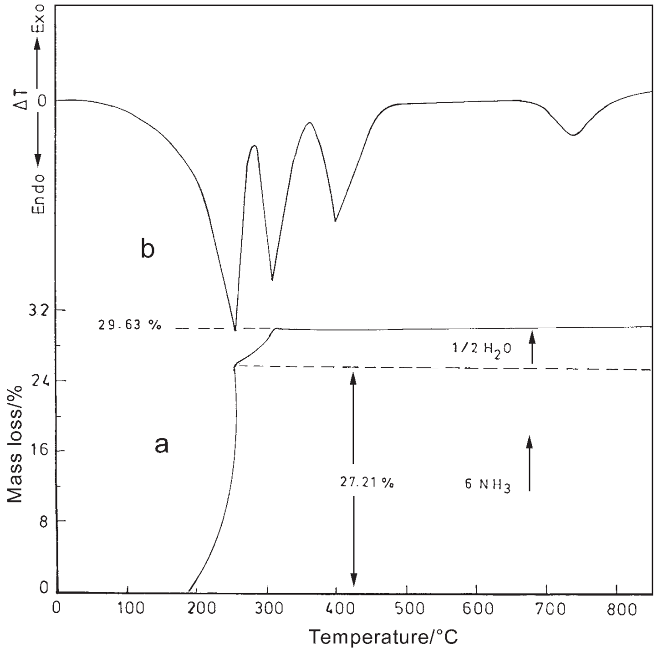

Fig. 4 Thermogravimetric (a) and differential thermal analysis (b) curves for $[Co(NH_3)_6][V_2O_6OH]$

IR study

The vibrational spectra of the formed ion-pair is characterized by the bands at 902, 805 cm^{-1} due to V=O stretching and at 705, 565 and 480 cm^{-1} due to V–O–V vibrations as shown in Table 2 and Fig. 5a. It is noticed as previously observed by Coomber and Griffith [21], that no appreciable changes take place in bonding inside either the cation or the anion forming the ion-pair.

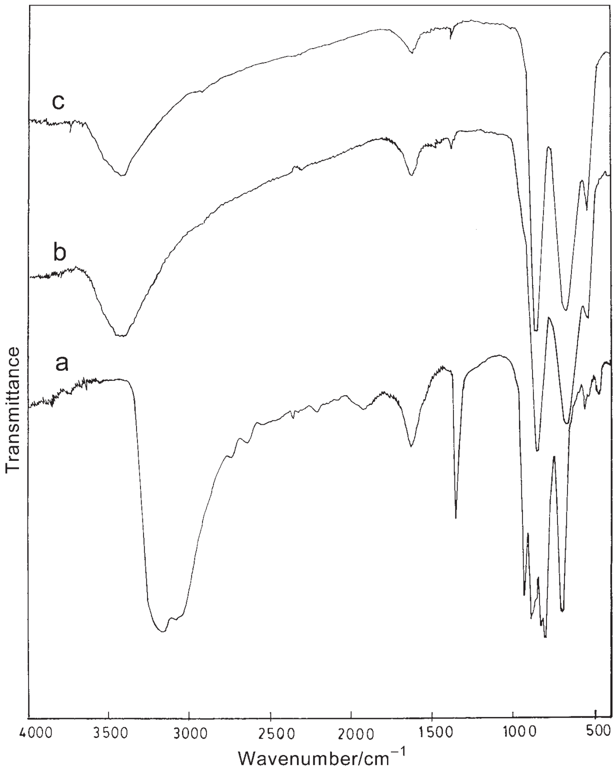

Fig. 5 Infrared spectra of a – [Co(NH$_3$)$_6$][V$_2$O$_6$OH]; b – the ion-pair heated at 260°C; c – the ion-pair heated at 400°C

On heating the ion-pair we could observe, (i) the disappearance of the NH$_3$ stretching band above 250°C (Fig. 5b), (ii) the shift of V=O bands originally occurring at 902, 804 and 704 cm^{-1}, to a new one at 859 cm^{-1} which is assigned to V=O in pure V$_2$O$_5$ and another band at 550 cm^{-1} assigned to V–O–V above 400°C [22] as shown in Fig. 5c.

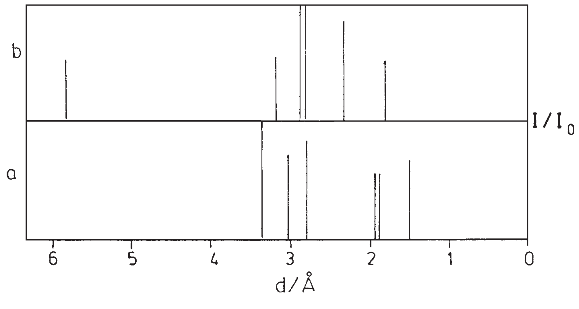

Fig. 6 XRD lines of a – [Co(NH$_3$)$_6$][V$_2$O$_6$OH] ion-pair; b – the ion-pair heated at 500°C

Compared with the results obtained on heating the ion-pair prepared at pH≈4, no reduction of Co(III) to Co(II) was observed in this case, the vibration band of Co(III)–O is observed at 678 cm^{-1} Fig. 5c.

X-ray analysis

Figure 6a shows the specific XRD lines of *d*-distances at 3.4, 3.05, 2.78, 1.91, 1.89 and 1.5 Å, in addition to that of the original ion [11]. On heating the formed ion-pair to 500°C for 1 h, XRD lines showed the characteristic lines of V_2O_5 [23] at *d*-distance equal 5.89, 3.23 and 2.89 Å and also that of Co_2O_3 at *d*-distance 2.78, 2.35 and 1.82 Å as shown in Fig. 6b.

Conclusions

Cobalt hexammine-vanadate ion-pairs complexes have been prepared; one in acid medium (pH≈4) and the other in alkaline medium (pH≈10). The formed complex in acid medium is of the formula $[Co(NH_3)_6]_5[HV_{10}O_{28}]_3\cdot18H_2O$ while that formed in alkaline medium is of the form $[Co(NH_3)_6][(V_2O_6OH]$. The formed complexes are characterized by their elemental analyses, IR and XRD techniques. The IR study suggests that the formed complexes are of the ion-pair type.

The thermogravimetric treatment of $[Co(NH_3)_6]_5[HV_{10}O_{28}]_3\cdot18H_2O$ is characterized by three main decomposition steps leaving the mixed oxides, CoO, V_2O_5 and VO_2 and thus showing the reduction of Co(III) to Co(II) and partial reduction of V(V). The thermal treatment of $[Co(NH_3)_6)][V_2O_6OH]$ is characterized by two main decomposition steps leaving mixture of Co_2O_3 and V_2O_5.

References

1 L. Shuncheng, S. N. Shaikh and J. Zubieta, Inorg. Chem., 26 (1987) 4303.
2 J. J. Cruywagen, J. B. Heyns and R. F. Van de Water, J. Chem. Soc. Dalton Trans., 9 (1986) 1857.
3 F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd Ed., (1972), p. 822.
4 C. M. Flynn, J. V. Pope and M. T. Pope, J. Am. Chem. Soc., 92 (1970) 85.
5 V. E. Mironov, G. I. Moshkova, A. K. Pyartman and N. P. Kolobov, Zb. Fiz. Khim., 50 (1976) 2995.
6 E. R. Souaya, W. G. Hanna and N. E. Milad, Thermochim. Acta, 143 (1989) 59.
7 R. Kozlowski, R. F. Pettifer and J. M. Thomas, J. Phys. Chem., 83 (1983) 5172.
8 J. Haber, A. Kowlowska and R. Kozlowski, J. Catal., 102 (1986) 52.
9 A. A. Said, J. Mater Sci., 27 (1992) 5869.
10 J. Bjerrum and J. P. McRynolds, Inorg. Synth., 2 (1966) 216.
11 T. V. Smith (ed.) X-ray powder data file and index to X-ray data file, ASTM Philadelphia, PA 1961.
12 ASTM Powder diffraction file, alphabetical index of inorganic phases, publ. by the International Center of Diffractions Data, Swarthmore, Pennsylvania, USA 1984.
13 The analytical uses of ethylene diamine tetraacetic acid, F. J. Welcher 1958, pp. 205 and 230.

14 L. H. Khalil, N. A. Moussa and S. Mikhail, J. Mater. Sci., 27 (1992) 567.
15 S. Kohata, M. Asakawa, T. Maeda, H. Shyo and A. Ohyoshi, Anal. Sci., 2 (1986) 325.
16 S. A. Selim, Ch. A. Philip and R. Sh. Mikhail, Thermochim. Acta, 36 (1980) 287.
17 P. K .Gallagher and C. R. Kurkjian, Inorganic Chem., 5 (1966) 214.
18 K. H. Schmidt and A. Müller, Coord. Chem. Rev., 19 (1976) 41.
19 P. C. H. Mitchell, J. Inorg. Nucl. Chem., 26 (1964) 1967.
20 M. Cousins and M. L. H. Green, J. Chem. Soc., (1964) 1567.
21 R. Coomber and W. P. Griffith, J. Chem. Soc. A, (1968) 1128.
22 K. Nakamoto, Infrared and raman spectra of inorganic and coordination compounds, 3rd Ed., 1978, p. 115.
23 A. A. Said and M. M. M. Abd El-Wahab, Thermochim. Acta, 249 (1995) 313.