Journal of Thermal Analysis and Calorimetry, Vol. 62 (2000) 737–745

# HYDRAZINIUM OXYDIACETATES AND OXYDIACETATE DIANION COMPLEXES OF SOME DIVALENT METALS WITH HYDRAZINE

*S. Yasodhai and S. Govindarajan*[*]

Department of Chemistry, Bharathiar University, Coimbatore 641 046, India

(Received June 26, 1999; in revised form March 20, 2000)

## Abstract

Hydrazinium oxydiacetate salts of formulae $N_2H_5(Hoda)\cdot H_2oda$, $N_2H_5(Hoda)$ and $(N_2H_5)_2oda$ ($H_2oda$= oxydiacetic acid) and complexes of the types, $M(oda)\cdot 2N_2H_4\cdot xH_2O$ (where $M$=Co, Ni and Cd; $x$=0 for Co and Ni; $x$=1 for Cd) and $Zn(oda)\cdot N_2H_4\cdot H_2O$ have been prepared and characterized by analytical, spectral, thermal and X-ray powder diffraction data. IR data document the existence of $N_2H_5^+$ ion in the simple salts and the bidentate coordination of both hydrazine and dianion in the complexes. Complete decomposition of hydrazinium salts takes place via oxydiacetic acid intermediate. Cobalt and nickel complexes decompose in a single step, whereas zinc and cadmium complexes decompose through hydrazinate intermediates. However, all the metal complexes yield metal oxide as the final residue. Isomorphic nature of the cobalt and nickel complexes is evident from XRD data.

**Keywords:** hydrazinium oxydiacetates, metal oxydiacetate hydrazinates, spectral studies, thermal decomposition

## Introduction

The synthesis and thermal decomposition of metal carboxylate hydrazinates have become a subject of recent interest, due to their wide use as precursors for fine particle metals or metal oxides [1–5]. The synthesis and characterization of such complexes have previously been reported from our laboratory with a few aliphatic carboxylates such as formate [6], acetate [7], propionate [8], malonate [7, 9] and succinate [10]. As compared to the aliphatic monocarboxylates, dicarboxylates [4, 9–12] show promising results due to their high exothermicity during decomposition. Oxydiacetic acid is an another class of dicarboxylic acid which can act as a versatile complexing agent with three oxygen donor atoms and can have a distinct affinity towards metal ions by forming up to five-membered chelate rings depending on the chemical environment. Though, variety of metal complexes of oxydiacetic acid is known with their crystal structures [13–17], there appears to be no report on metal hydrazine compounds of

---

[*] Author to whom all correspondence should be addressed.

*1418–2874/2000/ $ 5.00*

*Akadémiai Kiadó, Budapest*
*Kluwer Academic Publishers, Dordrecht*

oxydiacetic acid. Even, the simple salts of this acid with hydrazine are not known. Pursuing this objective, we herein report the preparation and characterization of hydrazinium oxydiacetates and oxydiacetate dianion complexes of Co(II), Ni(II), Zn(II) and Cd(II) with hydrazine.

## Experimental

All the chemicals used were of analytical grade and the solvents were freshly distilled before use. Hydrazine hydrate of 99–100% purity was used in all the reactions.

### *Preparation of hydrazinium salts*

Hydrazinium hydrogenoxydiacetate oxydiacetic acid and dihydrazinium oxydiacetate

Stoichiometric quantities of oxydiacetic acid (1.34 g, 0.01 mol ; 1.34 g, 0.01 mol) and hydrazine hydrate (0. 25 mL, 0.005 mol or 0.5 mL, 0.01 mol ; 1 mL, 0.02 mol, respectively) were mixed in 25 mL of water and heated to get clear solutions. The resulting solutions were allowed to crystallize in a vacuum desiccator over calcium chloride. Monohydrazinium salt was separated as white crystals after 5 days, whereas, spongy dihydrazinium salt was crystallized out only after a month. The salts were isolated from the solutions and washed with absolute alcohol and dried in *vacuo*, *m.p.* of $N_2H_5(Hoda)\cdot H_2oda$; 122°C; $(N_2H_5)_2oda$; 127°C.

Hydrazinium hydrogenoxydiacetate

Equimolar mixture of oxydiacetic acid (1.34 g, 0.01 mol) and hydrazine hydrate (0.5 mL, 0.01 mol) in 50 mL of ethanol yielded the titled product immediately. Then it was digested on a water bath for 5 min and the separation was done as above, *m.p.*: 130°C.

These salts are highly soluble in water and insoluble in alcohol.

Preparation of metal oxydiacetate hydrazinates

Oxydiacetic acid (0.67 g, 0.005 mol) and hydrazine hydrate (1 mL, 0.02 mol) in 25 mL of water was added to the respective aqueous solution (25 mL) of metal nitrate hydrates (e.g., $Co(NO_3)_2\cdot 6H_2O$, 1.46 g, 0.005 mol). The products separated were isolated and washed with water, alcohol and ether and dried in air. All the complexes are insoluble in water and alcohol and other organic solvents.

The hydrazine content in all the compounds was determined volumetrically using 0.025 M potassium iodate solution under Andrews' conditions [18]. The metal content was estimated by EDTA complexometric titration [18] after decomposing a known mass of the sample with concentrated nitric acid. Melting points were determined on Mettler FP 5 and are uncorrected. Magnetic measurements were carried out by the Guoy method using $Hg[Co(NCS)_4]$ as calibrant. The electronic spectra were obtained with a Shimadzu UV-Visible 240A instrument, performing absorption measurements through a filter paper impregnated with the Nujol suspension of the mate-

**Table 1** Analytical data

| Compound | Colour | Yield / % | Hydrazine | | Metal | | Carbon | | Hydrogen | | Nitrogen | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | found/ | calcd./ | found/ | calcd./ | found/ | calcd./ | found/ | calcd./ | found/ | calcd./ |
| | | | % | | | | | | | | | |
| $N_2H_5(Hoda)\cdot H_2oda$ | colourless | 80 | 10.66 | 10.67 | – | – | 31.87 | 32.00 | 05.19 | 05.33 | 09.22 | 09.33 |
| $N_2H_5(Hoda)$ | colourless | 70 | 19.30 | 19.28 | – | – | 28.85 | 28.92 | 06.00 | 06.02 | 16.82 | 16.87 |
| $(N_2H_5)_2oda$ | colourless | 75 | 32.10 | 32.65 | – | – | 24.19 | 24.24 | 06.96 | 07.07 | 28.03 | 28.28 |
| $Co(oda)\cdot 2N_2H_4$ | peach | 90 | 24.80 | 25.10 | 22.80 | 23.12 | 18.77 | 18.83 | 04.69 | 04.71 | 21.92 | 21.97 |
| $Ni(oda)\cdot 2N_2H_4$ | blue | 90 | 24.70 | 25.13 | 23.30 | 23.04 | 18.82 | 18.85 | 04.72 | 04.71 | 21.95 | 21.99 |
| $Zn(oda)\cdot N_2H_4\cdot H_2O$ | colourless | 90 | 12.50 | 12.94 | 26.10 | 26.43 | 19.45 | 19.40 | 04.09 | 04.04 | 11.30 | 11.32 |
| $Cd(oda)\cdot 2N_2H_4\cdot H_2O$ | colourless | 85 | 19.20 | 19.61 | 33.70 | 34.44 | 15.22 | 14.71 | 03.80 | 04.29 | 17.14 | 17.16 |

rial. Infrared spectra were recorded using KBr discs (4000–400 $cm^{-1}$) in a Shimadzu FTIR-8201PC spectrophotometer. The simultaneous TG-DTA studies were done on a STA 1500 thermal analyzer and the curves were obtained in air using platinum cups as sample holders with 5–10 mg of the samples at the heating rate of 10°C $min^{-1}$. The XRD patterns were recorded on a Siemens D 500 diffractometer with graphite secondary beam monochromator using $CuK_\alpha$ radiation.

## Results and discussion

### *Hydrazinium salts*

Dibasic acids with hydrazine are known to form $N_2H_4 \cdot 2H_2A$ ($N_2H_5HA \cdot H_2A$), $N_2H_4 \cdot H_2A$ ($N_2H_5HA$) or ($N_2H_6A$) and $2N_2H_4 \cdot H_2A$ ($(N_2H_5)_2A$) types of salts ($H_2A$ – dibasic acid). The hydrazinium salts of these types with different dibasic acids have been reported [19–21]. The best known of these are only $N_2H_4 \cdot H_2A$ and $2N_2H_4 \cdot H_2A$ with dicarboxylic acids. The hydrazinium salt of the type $N_2H_4 \cdot 2H_2A$ is quite rare and it is interesting to mention here that such a type of salt is obtained with oxydiacetic acid. A similar type of salt *viz*, sodium hydrogendipicolinate dipicolinic acid trihydrate has been reported [22] recently. Both 1:1 and 1:2 molar mixtures of base and acid in aqueous solutions yielded the same highly crystalline salt, $N_2H_5(Hoda) \cdot H_2oda$, whereas, equimolar mixture in alcoholic solution gave the powdered salt, $N_2H_5(Hoda)$.

The chemical analyses of these salts are consistent with the desired compositions (Table 1). The important infrared absorption bands of the acid and salts along with their band assignments are given in Table 2. The carbonyl stretchings of the free carboxyl groups of the salts are well comparable with oxydiacetic acid. All the salts show asymmetric and symmetric stretching frequencies of the carboxylate ions in the region 1610–1580 and 1440–1400 $cm^{-1}$, respectively. The N–N stretching frequency of the free $N_2H_5^+$ ion is known to occur in the region 990–950 $cm^{-1}$ [19]. The observed N–N stretching frequencies in the same range indicate the presence of $N_2H_5^+$ ion in these salts.

To know the decomposition of the compounds during pyrolysis, the simultaneous TG-DTA measurements of oxydiacetic acid and the hydrazinium salts have been carried out. The free acid melts (136°C) and decomposes endothermically at 250°C to give ethylene as a probable intermediate which further undergoes a complete exothermic decomposition in the range 254–390°C.

The TG-DTA studies of the salts indicate that they decompose completely in three steps through oxydiacetic acid and ketene intermediates. Melting with dehydrazination take place in the first step endothermically in the range 130–168°C, thereby giving oxydiacetic acid as an intermediate. Oxydiacetic acid on disproportionation in the second step forms ketene as the final intermediate. Ketenes are known to be formed by the pyrolysis of carboxylic acids and acid anhydrides [23]. The slow decomposition of ketene, as observed from both TG and DTA results shows the formation of polymerized product of ketene. It is informed that polymers decompose slowly [24] without any sharp thermal transformation. Though the three salts have different compositions, they decompose in the same temperature ranges (Table 3) which authenticate the similar pattern of decompositions and the formation of same intermediates.

Our effort to isolate the intermediates was unsuccessful due to their continuous decomposition. Hence, we have tried to assign the possible intermediates as observed from the TG mass losses which are well consistent with the calculated mass losses (Table 3).

**Table 2** Infrared data (4000–400 cm$^{-1}$)

| Compound | ν(O–H) | ν(N–H) | ν(C=O) | $\nu_{asym}$(COO) | $\nu_{sym}$(COO) | ν(N–N) |
|---|---|---|---|---|---|---|
| $H_2$oda | 3030 | – | 1732 | – | – | – |
| $N_2H_5$(Hoda)·$H_2$oda | 3220 | 3000 | 1732 | 1580 | 1440 | 953 |
| $N_2H_5$(Hoda) | 3480<br>3300 | 3210 | 1751 | 1610 | 1406 | 955 |
| $(N_2H_5)_2$oda | –<br>– | 3420<br>3380<br>3200 | – | 1585 | 1410 | 960 |
| Co(oda)·$2N_2H_4$ | – | 3338<br>3286<br>3190 | – | 1640<br>1610 | 1426<br>1402 | 964 |
| Ni(oda)·$2N_2H_4$ | – | 3340<br>3284<br>3190 | – | 1640<br>1612 | 1426<br>1404 | 964 |
| Zn(oda)·$N_2H_4$·$H_2O$ | 3500<br>3400 | 3255<br>3153 | –<br>– | 1638<br>1600 | 1440<br>1412 | 984 |
| Cd(oda)·$2N_2H_4$·$H_2O$ | 3600<br>3400 | 3285<br>3225<br>3148 | – | 1602<br>1562 | 1410<br>1385 | 960 |

### *Metal oxydiacetate hydrazinates*

Reactions of aqueous solutions of the simple salts with metal ions, in appropriate ratios, did not yield any desired product. Hence, an aqueous mixture containing oxydiacetic acid and hydrazine hydrate in 1:4 molar ratio was used as such for the preparation of the complexes. The analytical data of the complexes are in good agreement with the proposed compositions of the complexes (Table 1).

The magnetic moment values of the cobalt and nickel complexes, 4.5 and 2.9 BM, respectively, are in accordance with the high spin octahedral nature of the complexes [25]. As expected, the zinc and cadmium complexes are diamagnetic.

**Table 3** Thermal data

| Compound | DTA peak temperature/°C | Thermogravimetry (TG) |  |  | Intermediate / final product |
|---|---|---|---|---|---|
|  |  | temperature range/°C | mass loss found | mass loss calcd. |  |
| $H_2$oda | 136(+) | – | – | – | melting |
|  | 250(+) | 200–254 | 80.00 | 79.10 | ethylene |
|  | 370(–) | 254–390 | 98.00 | 100.00 | complete decomposition |
| $N_2H_5$(Hoda)·$H_2$oda | 142(+)$^{m,d}$ | 137–168 | 11.20 | 10.67 | $H_2$oda |
|  | 265(–) | 168–278 | 74.00 | 72.00 | ketene |
|  | 324(–) |  |  |  |  |
|  | 405(–) |  |  |  |  |
|  | 482(–)$^{CBM}$ | 278–542 | 92.00 | 100.00 | complete decomposition |
| $N_2H_5$(Hoda) | 134(+)$^{m,d}$ | 130–153 | 18.00 | 19.28 | $H_2$oda |
|  | 288(–) | 153–290 | 74.00 | 74.70 | ketene |
|  | 357(–) |  |  |  |  |
|  | 410(–) |  |  |  |  |
|  | 482(–)$^{CBM}$ | 290–530 | 98.00 | 100.00 | complete decomposition |
| $(N_2H_5)_2$oda | 132(+)$^{m}$ | 130–168 | 28.00 | 32.32 | $H_2$oda |
|  | 155(–)$^{D}$ |  |  |  |  |
|  | 280(–) |  |  |  |  |
|  | 407(–) |  |  |  |  |
|  | 480(–) | 168–280 | 75.00 | 78.79 | ketene |
|  | 580(–)$^{CBM}$ | 280–580 | 95.00 | 100.00 | complete decomposition |
| Co(oda)·$2N_2H_4$ | 279(–) |  |  |  |  |
|  | 296(–)$^{D}$ | 262–330 | 65.00 | 68.52 | $Co_3O_4$ |
| Ni(oda)·$2N_2H_4$ | 284(–) |  |  |  |  |
|  | 296(–) |  |  |  |  |
|  | 321(–)$^{T}$ | 260–350 | 70.00 | 70.67 | NiO |
| Zn(oda)·$N_2H_4$·$H_2O$ | 50(+) | 30–65 | 05.00 | 07.28 | Zn(oda)·$N_2H_4$ |
|  | 270(–) | 210–290 | 15.00 | 13.74 | Zn(oda)·$0.5N_2H_4$ |
|  | 418(–) | 290–450 | 64.00 | 67.10 | ZnO |
| Cd(oda)·$2N_2H_4$·$H_2O$ | 72(+) | 50–80 | 04.10 | 05.51 | Cd(oda)·$2N_2H_4$ |
|  | 182(+) | 120–210 | 10.00 | 10.42 | Cd(oda)·$1.5N_2H_4$ |
|  | 300(–) | 210–310 | 19.00 | 20.22 | Cd(oda)·$0.5N_2H_4$ |
|  | 374(–) | 310–415 | 55.00 | 60.00 | CdO |

(+): endothermic; (–): exothermic; d: decomposition; CBM: complex broad multiplet; D: doublet; T: triplet

The electronic absorption spectrum of cobalt dihydrazinate shows bands at 19.084 and 20.410 $cm^{-1}$ which are assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition and usually splits due to the spin-orbit coupling in the $^4T_{1g}(P)$ state. The nickel dihydrazinate shows two bands at 17.858 and 29.240 $cm^{-1}$ which are ascribable to the transitions $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, respectively. These transitions are characteristics of octahedral geometry of the metal atoms [26].

The important infrared absorption frequencies are listed in Table 2. A broad band in the region 3600–3400 $cm^{-1}$ due to O–H stretching in the zinc and cadmium complexes shows the presence of water molecule. This is further borne out by the thermal decomposition data. The oxydiacetate dianion in these complexes coordinate to the metal as a bidentate ligand via both the carboxylate groups. Both the asymmetric and symmetric stretchings of carboxylate ions split into two bands in the regions around 1640–1600, 1610–1580, and 1440–1410, 1410–1385 $cm^{-1}$, respectively, with $\Delta\nu(\nu_{asy}-\nu_{sym})$ separation of above 170 $cm^{-1}$ indicating the monodentate coordination of both carboxylate groups in the dianion. The N–N stretching frequencies observed in the range 985–960 $cm^{-1}$ for all the complexes document clearly that the hydrazine molecules are present as bridging bidentate ligands [27].

The TG and DTA data of the complexes are summarized in Table 3. The TG and DTA show that all the complexes yield metal oxide as the final residue. The cobalt and nickel complexes decompose exothermically in a single step, whereas the zinc and cadmium complexes decompose via hydrazinate intermediates after dehydration. The low temperature dehydration confirms the presence of water molecule as a lattice water.

The decomposition reactions in air, on the basis of the mass losses in the TG curves, can be written as follows:

1. $3Co(oda){\cdot}2N_2H_4 \xrightarrow[262-330\,°C]{exo} Co_3O_4+N_2+NH_3+CO_2+H_2O$

2. $Ni(oda){\cdot}2N_2H_4 \xrightarrow[260-350\,°C]{exo} NiO+N_2+NH_3+CO_2+H_2O$

3. $Zn(oda){\cdot}2N_2H_4{\cdot}H_2O \xrightarrow[30-65°C]{endo} Zn(oda){\cdot}N_2H_4+H_2O$ (i)

$Zn(oda){\cdot}N_2H_4 \xrightarrow[210-290\,°C]{exo} Zn(oda){\cdot}0.5N_2H_4+N_2+NH_3$ (ii)

$Zn(oda){\cdot}0.5N_2H_4 \xrightarrow[290-450\,°C]{exo} ZnO+N_2+NH_3+CO_2+H_2O$ (iii)

4. $Cd(oda){\cdot}2N_2H_4{\cdot}H_2O \xrightarrow[50-80\,°C]{endo} Cd(oda){\cdot}2N_2H_4+H_2O$ (i)

$Cd(oda){\cdot}2N_2H_4 \xrightarrow[120-210\,°C]{endo} Cd(oda){\cdot}1.5N_2H_4+N_2+NH_3$ (ii)

$Cd(oda){\cdot}1.5N_2H_4 \xrightarrow[210-310\,°C]{exo} Cd(oda){\cdot}0.5N_2H_4+N_2+NH_3$ (iii)

$Cd(oda){\cdot}0.5N_2H_4 \xrightarrow[310-415°C]{exo} CdO+N_2+NH_3+CO_2+H_2O$ (iv)

In order to know the isomorphic nature among the complexes, the X-ray powder patterns have been compared (Table 4). The complexes of cobalt and nickel show similar values of ‘d’ spacings suggesting isomorphism between the two.

**Table 4** X-ray powder diffraction data (d-spacings/Å)

| Co(oda)·$2N_2H_4$ | Ni(oda)·$2N_2H_4$ | Zn(oda)·$N_2H_4$·$H_2O$ | Cd(oda)·$2N_2H_4$·$H_2O$ |
|---|---|---|---|
| 8.31 | 8.23 | 11.78 | 7.80 |
| 6.26 | 6.17 | – | 6.35 |
| – | – | – | 6.07 |
| – | – | 5.06 | 5.95 |
| 4.61 | 4.59 | – | 4.73 |
| 4.08 | – | – | 4.13 |
| 3.86 | 3.86 | – | – |
| 3.43 | 3.36 | 3.32 | 3.44 |
| 3.06 | 3.02 | – | 3.14 |
| 2.77 | 2.78 | 2.84 | 2.88 |
| 2.50 | 2.47 | – | 2.54 |
| 2.30 | 2.28 | 2.17 | 2.27 |
| 1.87 | 1.86 | – | 2.08 |
| 1.73 | 1.71 | – | 1.71 |

The cobalt, nickel and cadmium complexes are dihydrazinates, whereas zinc is monohydrazinate as evidenced from analytical and thermal data. The analytical and physico–chemical studies suggest that the hydrazine molecules are present as a bridging bidentate and the oxydiacetate dianion as a bidentate ligands. The complexes are isolated only as polycrystalline powders. Hence, without crystal structure, it is very difficult to predict the environment of the metal ions. However, magnetic moments and electronic spectral data suggest octahedral geometry for the cobalt and nickel complexes. The monohydrazinate zinc and dihydrazinate cadmium compounds seem to prefer four and six coordinations with tetrahedral and octahedral geometries, respectively. The insoluble nature of these complexes conforms to the polymeric structure.

Thus, it is interesting to note that oxydiacetic acid differs from other dicarboxylic acids [21] in terms of its salt forming ability, but shows similarity towards complexation.

* * *

S. Yasodhai thanks the Council of Scientific and Industrial Research, New Delhi, India, for the award of a Senior Research Fellowship. We thank Indira Gandhi Centre for Atomic Research, Kalpakkam, Chennai for providing XRD data.

## References

1 F. J. Arnaiz Garcia, An. Quim., 73 (1977) 1121.
2 G. V. Mahesh and K. C. Patil, Thermochim. Acta, 99 (1986) 188.
3 P. Ravindranathan and K. C. Patil, Am. Ceram. Soc. Bull., 66 (1987) 688.
4 D. Gajapathy, K. C. Patil and V. R. Pai Verneker, Mat. Res. Bull., 17 (1982) 29.
5 K. C. Patil, Bull. Mater. Sci., 16 (1993) 533.
6 B. N. Sivasankar and S. Govindarajan, Synth. React. Inorg. Met.-org. Chem., 25 (1995) 31.
7 B. N. Sivasankar and S. Govindarajan, J. Thermal Anal., 48 (1997) 1401.
8 B. N. Sivasankar and S. Govindarajan, Z. Naturforsch., 49b (1994) 950.
9 B. N. Sivasankar and S. Govindarajan, Mat. Res. Bull., 31 (1996) 47.
10 B. N. Sivasankar and S. Govindarajan, Synth. React. Inorg. Met.-org. Chem., 24 (1994) 1573.
11 K. C. Patil, D. Gajapathy and K. Kishore, Thermochim. Acta, 52 (1982) 113.
12 S. Govindarajan, S. U. Nasrin Banu, N. Saravanan and B. N. Sivasankar, Proc. Indian Acad. Sci. (Chem. Sci.), 107 (1995) 559.
13 S. H. Whitlow and G. J. Davey, J. Chem. Soc. Dalton Trans., (1975) 1228.
14 R. Baggio, M. T. Garland, M. Perec and D. Vega, Inorg. Chem., 34 (1995) 1961.
15 R. Baggio, M. T. Garland, M. Perec and D. Vega, Inorg. Chem., 35 (1996) 2396.
16 R. Baggio, M. T. Garland, M. Perec and D. Vega, Inorg. Chem., 36 (1997) 950.
17 G. Svensson, S. Olson and J. Albertsson, Acta. Chem. Scand., 52 (1998) 868.
18 I. A. Vogel, A Textbook of Quantitative Inorganic Analysis, Longmans Green, London 1975, pp. 380 and 433.
19 E. W. Schmidt, Hydrazine and its Derivatives - Preparation, Properties and Applications, Wiley Interscience, New York 1984.
20 D. Gajapathy, S. Govindarajan and K. C. Patil, Thermochim. Acta, 60 (1983) 87.
21 K. Kuppusamy, B. N. Sivasankar and S. Govindarajan, Thermochim. Acta, 259 (1995) 251.
22 K. Browning, K. A. Abboud and G. J. Palenik, J. Chem. Crystallogr., 25 (1995) 851.
23 T. T. Tidwell, Ketenes 1995.
24 K. C. Patil, J. P. Vittal and C. C. Patel, Proc. Indian Acad. Sci. (Chem. Sci.), 89 (1980) 87.
25 B. N. Figgis and J. Lewis, J. Prog. Inorg. Chem., 6 (1964) 197.
26 A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam 1984.
27 A. Braibanti, F. Dallavalle, M. A. Pellinghelli and E. Leporati, Inorg. Chem., 7 (1968) 1430.