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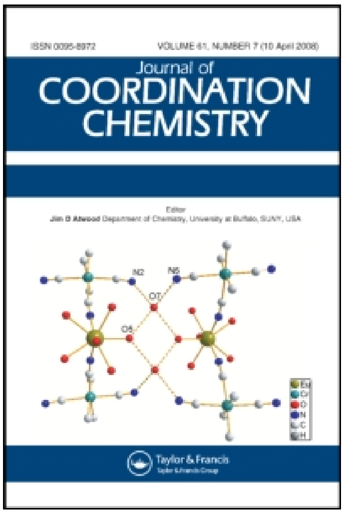

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# SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF AN OXOVANADIUM(V) COMPLEX WITH THE SCHIFF BASE *N*-BENZOYLACETONE-*M*-CHLOROBENZOYLHYDRAZONE

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# SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF AN OXOVANADIUM(V) COMPLEX WITH THE SCHIFF BASE *N*-BENZOYLACETONE-*M*-CHLOROBENZOYLHYDRAZONE

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The reaction of $(n\text{-}C_4H_9)_4NVO_3$ with the Schiff base *N*-benzoylacetone-*m*-chlorobenzoylhydrazone ($H_2L$) in absolute ethanol solution affords the title complex, which has been characterized by elemental analysis, EPR, IR, $^1$H NMR, electronic absorption spectra and TGA studies. EPR and electronic absorption spectra confirm that the oxidation state of vanadium is + 5. Black crystals of the complex are triclinic, space group $P\bar{1}$ with $a = 7.392(3)$, $b = 11.229(4)$, $c = 11.719(4)$Å, $\alpha = 83.20(3)$, $\beta = 76.54(3)$, $\gamma = 87.84(4)°$, $V = 939.2(8)$Å$^3$, $F(000) = 438$ and $D_c = 1.505$ g cm$^{-3}$ for $Z = 2$. The X-ray structure analysis reveals that the vanadium(V) coordination number is five and the coordination polyhedron is a square pyramid.

KEYWORDS: oxonvandium(V), Schiff base, terdentate, crystal structure

## INTRODUCTION

In recent years, there has been considerable interest in the coordination chemistry of vanadium in view of its special structural, catalytic and biological effects.[1-6] While our awareness of the occurrence of vanadium in biological systems is increasing,[7] an understanding of its structures, functional and mechanistic properties therein is still a current topic of research. The oxidation state of vanadium in biological environments is commonly presumed to be IV; accumulating evidence suggests that vanadium(V) is also present.[5] For example, the bromoperoxidases, which catalyze the reaction shown in (*1*), are thought to contain a mononuclear vanadium(V) active site.[8]

$$AH + B_r^- + H_2O_2 + H^+ \rightarrow AB_r + 2H_2O \qquad (1)$$

A mechanism of bromination of organic substrates by these haloperoxidases has been proposed by Clague *et al.*[9] They reported two functional mimics of the

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vanadium bromoperoxidase, the vanadium(V) complexes LVO(OEt)(EtOH) and L*VO(OEt)(EtOH), where $H_2L$ = *N*-(2-hydroxyphenyl)salicylideneamine and $H_2L^*$ = *N*-(2-carboxyphenyl)salicylideneamine. The two complexes catalyze the oxidation of bromide by hydrogen peroxide in organic medium, analogous to the aqueous reaction of vanaium bromoperoxidase. It was suggested that the $V^V$-catalyzed oxidation of halides by hydrogen peroxide may be a fairly general property of the oxovanadium(V) moiety.

In the present paper, we describe the synthesis, structure and spectroscopic characterization of oxovanadium(V) with a new terdentate Schiff base which is similar to that reported in a previous paper.[10] A comparison of related vanadium(V) complexes is made.

## EXPERIMENTAL

### *Materials and Measurements*

Benzoylacetone was obtained from BDH. All other reagent grade chemicals and reagents were purchased commercially and used without further purification. The salt $(n\text{-}C_4H_9)_4NVO_3$ was synthesized according to the literature.[11] The Schiff base ligand $H_2L$ was prepared by condensing benzolacetone with stoichiometric quantities of *m*-chlorobenzoylhydrazide in the usual way.[10] Elemental analyses were performed on an Italy 1106 apparatus. IR spectra were recorded in KBr discs on a Nicolet 170SX spectrophotometer. Electronic spectra were measured on a Shimadzu UV-260 instrument. Thermal behavior was studied using a Dupont 1090 apparatus. $^1H$ NMR spectra were recorded on a Varian FT-80A spectrometer. Single crystal X-ray data were collected on an automatic Enraf-Nonius CAD-4 diffractometer.

### $[VO(m\text{-}ClC_6H_4C(O)NNC(CH_3)CHC(O)C_6H_5)(OCH_2CH_3)]$

Solid $(n\text{-}C_4H_9)_4NVO_3$ (170.7 mg, 0.5 mmol) was added to an absolute ethanol solution of $H_2L$ (157.4 mg, 0.5 mmol). The reaction mixture was heated to reflux and stirred for 2h. The resulting black solution was cooled to room temperature and allowed to stand for 2–3 days, when fine black cyrstals of the title complex were obtained. They were suitable for X-ray analysis. Yield: 80%. Found: C, 53.85; N, 6.76; H, 4.31%; Calc. for $C_{19}H_{18}ClN_2O_4V$:C,53.73; N,6.60; H,4.27.

### *Crystal structure determination*

A single crystal with approximate dimensions 0.15x0.25x0.30 mm was mounted on a glass fibre. Intensity data were collected on an Enraf-Nonius diffractometer with graphite-monochromated Cu-$K_\alpha$ radiation ($\lambda$ = 1.54184Å) using the $\omega$-$2\theta$ scan mode [scan width: $0.6 + 0.14\tan\theta$]. Some 2481 independent reflections were collected in the range $2 \leq 2\theta \leq 110°$, 2070 of which with $I \geq 3\sigma(I)$ were used for further computation.

### *Crystal data*

$C_{19}H_{18}ClN_2O_4V$, $M = 424.75$, triclinic, space group $P\bar{1}$, $a = 7.392(3)$, $b = 11.229(4)$, $c = 11.719(4)$Å, $\alpha = 83.20(3)°$, $\beta = 76.54(3)°$, $\gamma = 87.84(4)°$, $V = 939.2(8)$Å$^3$, $D_c = 1.505$ g cm$^{-3}$, $Z = 2$, $\mu$(Cu-K$_\alpha$) = 60.421 cm$^{-1}$, $F(000) = 438$.

The structure analysis was performed on a PDP 11/44 computer with the SDP program.[12] The position of the vanadium atom was determined by direct methods. The other non-hydrogen atoms were revealed by difference Fourier syntheses. The positions of the hydrogen atoms were calculated as idealized contributions and the structure was refined by full-matrix least-squares methods to final $R = 0.074$, $R_w = 0.077$ (unit weights). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

## RESULTS AND DISCUSSION

### *Crystal structure studies*

Atomic coordinates of non-hydrogen atoms and isotropic thermal parameters are given in Table 1. Selected bond lengths and angles are listed in Table 2. The molecular structure of the title complex is shown in Figure 1. The X-ray analysis establishes that the title complex is a monomeric oxovanadium(V) species with

**Table 1** Atomic coordinates and thermal parameters for the non-hydrogen atoms of the complex.

| Atom | *x/a* | *y/b* | *z/c* | *Beq* |
|---|---|---|---|---|
| V | 0.9045(2) | 0.0220(2) | 0.2505(1) | 3.60(4) |
| Cl | 1.3559(5) | -0.3566(3) | -0.1655(3) | 7.53(8) |
| O1 | 0.7058(9) | 0.0366(7) | 0.2182(6) | 5.8(2) |
| O2 | 1.0298(9) | -0.1083(5) | 0.1763(5) | 4.6(1) |
| O3 | 0.8858(8) | 0.1047(6) | 0.3789(5) | 4.3(1) |
| O4 | 1.057(1) | 0.1226(6) | 0.1484(6) | 6.5(2) |
| N1 | 0.8998(9) | -0.2368(7) | 0.3365(6) | 3.8(2) |
| N2 | 0.8479(9) | -0.1236(6) | 0.3748(5) | 3.4(2) |
| C1 | 1.165(1) | -0.2929(9) | 0.0420(8) | 4.3(2) |
| C2 | 1.238(1) | -0.3860(9) | -0.0178(8) | 4.8(2) |
| C3 | 1.221(2) | -0.504(1) | 0.031(1) | 6.0(3) |
| C4 | 1.124(2) | -0.528(1) | 0.147(1) | 6.3(3) |
| C5 | 1.049(1) | -0.435(1) | 0.2096(9) | 5.4(3) |
| C6 | 1.069(1) | -0.3168(8) | 0.1603(7) | 3.9(2) |
| C7 | 0.994(1) | -0.2179(8) | 0.2270(7) | 3.8(2) |
| C8 | 0.760(1) | -0.1262(8) | 0.4860(7) | 3.5(2) |
| C9 | 0.709(1) | -0.0194(9) | 0.5355(7) | 4.2(2) |
| C10 | 0.770(1) | 0.0913(8) | 0.4860(7) | 3.5(2) |
| C11 | 0.719(1) | 0.2023(8) | 0.5385(7) | 3.4(2) |
| C12 | 0.775(1) | 0.3110(9) | 0.4738(8) | 4.6(2) |
| C13 | 0.723(1) | 0.4183(9) | 0.5189(9) | 5.4(3) |
| C14 | 0.615(1) | 0.419(1) | 0.6305(9) | 5.8(3) |
| C15 | 0.556(1) | 0.309(1) | 0.6959(8) | 5.2(3) |
| C16 | 0.607(1) | 0.2037(9) | 0.6519(8) | 4.4(2) |
| C17 | 0.709(1) | -0.2448(9) | 0.5618(8) | 4.7(2) |
| C18 | 1.271(2) | 0.122(2) | 0.119(1) | 10.4(5) |
| C19 | 1.333(2) | 0.146(2) | 0.002(1) | 11.9(6) |

*$Beq = 4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

**Table 2** Selected bond distances (Å) and angles(°) for the complex.

| | | | |
|---|---|---|---|
| | Distances(Å) | | |
| V-O1 | 1.598(5) | O4-C18 | 1.538(12) |
| V-O2 | 1.893(5) | N1-N2 | 1.409(7) |
| V-O3 | 1.835(5) | N1-C7 | 1.307(8) |
| V-O4 | 1.770(4) | N2-C8 | 1.310(8) |
| V-N2 | 2.043(6) | C8-C9 | 1.396(9) |
| O2-C7 | 1.310(8) | C8-C17 | 1.519(9) |
| O3-C10 | 1.339(7) | C9-C10 | 1.355(9) |
| | Angles(°) | | |
| O1-V-O2 | 107.7(3) | N1-N2-C8 | 114.9(5) |
| O1-V-O3 | 105.4(2) | O2-C7-N1 | 120.3(6) |
| O1-V-O4 | 107.3(3) | O2-C7-C6 | 118.3(6) |
| O1-V-N2 | 98.4(2) | N1-C7-C6 | 121.3(6) |
| O2-V-O3 | 142.6(2) | N2-C8-C9 | 120.2(6) |
| O2-V-O4 | 89.7(2) | N2-C8-C17 | 120.8(7) |
| O2-V-N2 | 74.7(2) | C9-C8-C17 | 119.1(6) |
| O3-V-O4 | 96.6(2) | C8-C9-C10 | 125.5(7) |
| O3-V-N2 | 83.9(3) | O3-C10-C9 | 119.9(6) |
| O4-V-N2 | 153.2(2) | O3-C10-C11 | 114.7(6) |
| N2-N1-C7 | 107.0(5) | C9-C10-C11 | 125.4(6) |

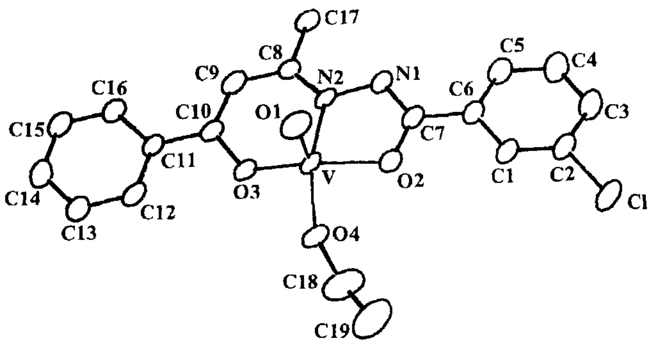


**Figure 1** A view of the $[V^VO(L)(OCH_2CH)]$ molecule showing atom numbering. Hydrogen atoms have been omitted for clarity.

formula $[V^VO(L)(OCH_2CH_3)]$. Since the monoxovanadium(V) entity, analogous to oxomolybdenum(V), is rare[13] in comparison to dioxovanadium(V) species, the present structure is quite characteristic. In the structure, the Schiff base $H_2L$ functions as a dibasic terdentate ligand in the enol form and bonds to the $VO^{3+}$ core through the ONO donor set. Thus, the metal is in a five-coordinate square-pyramidal geometry with the terdentate Schiff base and an ethoxide ion occupying the basal positions. Chelation gives rise to one five- and one six-membered ring. As a whole, the molecule is composed of four coplanar rings, which make the structure very stable. The vanadyl $V^V = O$ distance [1.598(5)Å] is almost the same as that [1.598(4)Å] and [1.591(4)Å] in the compound $[VO(SALAMHP)]_2O$ reported by Carrano *et al.*[14] However, the value is lower than that [1.616(3), 1.601(3)Å] reported for $[VO_2(BAP)]$,[10] and higher than that [1.579(4)Å] reported for [$V^VO(sal\text{-}L\text{-}ala)(OCH_3)(CH_3OH)$].[15] It seems that the V = O bond length is scarcely influenced by the oxidation state of the vanadium ion,[15] and mainly influenced by the geometry around the vanadium ion. The bond distances V-O2 [1.893(5)Å] and V-O3 [1.835(5)Å] are in the range reported in the literature.[16] Bond lengths V-N2 2.043(6)Å and V-O4 1.770(4)Å are similar to those in analogues.[15] N1-C7[1.307(8)Å] and N2-C8[1.310(8)Å] distances indicate that these correspond to double bonds.[10] The bond angles in the basal plane O2-V-N2 74.7(2)°, N2-V-O3 83.9(3)°, O4-V-O2 89.7(2)° are smaller than the regular angle 90° with the exception of O3-V-O4 96.6(2) °, whereas the vertex angles O1-V-O2 107.7(3)°, O1-V-N2 98.4(2)°, O1-V-O3 105.4(2)°, O1-V-O4 107.3(3)° are larger than 90° as a result of the central vanadium being displaced toward the vanadyl oxygen by 0.482Å from the best least-squares plane defined by O2, O3, O4, and N2. The torsion angles C6-C7-N1-N2, C7-N1-N2-C8, C9-C8-N2-N1 and C8-C9-C10-C11 are −180.0(8), −176.3(7), 177.4(7) and −179.0(8)°, respectively.

### *Comparison of Structures of Related Vanadium(V) Complexes*

In previous papers,[10,17] we have reported that *cis*-dioxovanadium(V) monomers [$VO_2$(Sal-P)]·$CH_3OH$(*I*), [$VO_2$(Sal-T)](*II*) and [$VO_2$(BAP)]·$C_2H_5OH$ (*III*) that have very similar coordination environments to that of the title complex [$VOL(OC_2H_5)$] (*IV*). In these complexes, the Schiff bases all act as terdentate donors coordinating through ONO and form a distorted square pyramid configuration in complex *I* and *IV* and a distorted trigonal bipyramid configuration in *II* and *III*. The main difference between the title and reported complexes is that the vanadium(V) exists as $VO^{3+}$ in the title complex and as $VO_2^+$ in the other complexes. Clague's complex, LVO(OEt)(EtOH)(*V*) also has a similar (ONO) Schiff base. Although vanadium(V) exists as $VO^{3+}$ in *IV* and *V*, the vanadium coordination number is different due to the two kinds of Schiff bases. A five-coordinate square pyramid geometry in complex *IV* and a six-coordinate octahedral geometry in complex V, respectively, results.

### *Spectroscopic studies*

IR data for the ligand $H_2L$ and its complex are listed in Table 3. The υV = O band around 995 $cm^{-1}$ is observed in the complex, indicating the high π-bond order of vanadium-oxygen bond of $VO^{3+}$ and the presence of monometric oxovanadium species.[18,19] The band due to υC = O in the free ligand at 1682 $cm^{-1}$ disappears in the spectrum of the complex, suggesting enolization of the ligand and reaction of the enol form with elimination of two protons. A new band at 1232 $cm^{-1}$ may be due to the enolic υC-O. The characteristic υC = N ligand band at 1514 $cm^{-1}$ displays a shift to higher frequency (1546 $cm^{-1}$), indicating coordination of the azomethine nitrogen to vanadium. The reason for the lower frequency of υC = N compared with those of [$VO_2$(BAP)] and [$VO_2$(sal-P/T)][17] is that the whole molecule is a conjugated system. The ligand band υNH at 3263 $cm^{-1}$ is absent. The presence of a new band at 1039 $cm^{-1}$ is due to the υC-O vibration of the ethoxide ion coordinated to the vanadium. Additional υV-O and υV-N bands at 526 and 359 $cm^{-1}$ appear after complexation.

Electronic absorption spectra were measured in $CH_3CN$. The ligand $H_2L$ exhibits three electronic absorption bands at 227.4 nm ($\varepsilon = 7.91\times10^3$ $M^{-1}cm^{-1}$), 278.8 nm

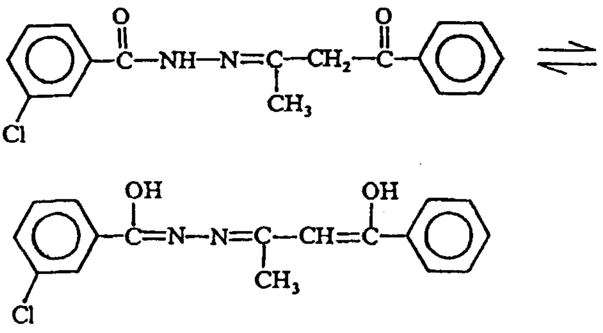
**Table 3** IR and ¹NMR data for the ligand and the complex.

| | IR($cm^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | υC = O | υC = N | υN-H | υC-O (enolic) | υC-O (ethoxide) | υV = O | υV-O | υV-N |
| $H_2L$ | 1682 | 1514 | 3263 | | | | | |
| $[V^VO(L)(OCH_2CH_3]$ | | 1546 | | 1232 | 1039 | 995 | 526 | 359 |
| | $^1H$ NMR (δ ppm) | | | | | | | |
| | phenyl | sub.phenyl | -NH- | $-CH_2-$ | -CH = | $-CH_3$ | $-OCH_2-$ | $-CH_3$ (ethoxide) |
| $H_2L$ | 7.44–7.27 | 7.96–7.80 | 5.34 | 3.17 | | 2.09 | | |
| $[V^VO(L)(OCH_2CH_3)]$ | 7.60–7.19 | 8.09–7.98 | | | 3.74 | 2.17 | 1.77–1.49 | 1.35–1.18 |

($\varepsilon = 1.78\times10^3\ M^{-1}cm^{-1}$) and 328.4 nm ($\varepsilon = 2.88\times10^3\ M^{-1}cm^{-1}$), which may be due to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions. The three bands shift to 224.0 nm ($\varepsilon = 2.21\times10^4\ M^{-1}cm^{-1}$), 290.6 nm ($\varepsilon = 2.00\times10^4\ M^{-1}cm^{-1}$) and 363.8 nm ($\varepsilon = 1.35\times10^4\ M^{-1}cm^{-1}$), respectively, upon coordination of the Schiff base to vanadium. The absence of d-d transitions in the visible region is expected. In addition, the title complex is EPR inactive in the solid state. These facts too indicate that the oxidation state of vanadium is + 5.

$^1H$ NMR spectra of the ligand and its complex have been recorded in $CDCl_3$ using $SiMe_4$ as internal standard. Data are listed in Table 3. The spectrum of the free ligand exhibits an NH resonance at 5.34 ppm, $-CH_2-$ protons at 3.17 ppm, $-CH_3$ protons at 2.09 ppm, phenyl and substituted phenyl protons at 7.44 - 7.27 and 7.96 - 7.80 ppm, respectively. On coordination, these signals move downfield with respect to the free ligand. The signal for the NH proton disappears.

All of the above characteristics support the crystallographically determined structure of the complex. The ligand in ketonic form converts to the enol form on coordination (Scheme 1).



**Scheme 1**

### *TGA studies*

The ligand melts at 105°C, then decomposes from 156 to 335°C with a sharp endothermic peak at 250°C. Three consecutive steps are observed in the thermal decomposition of the complex. The first weight loss (10.5%) at 135 – 226°C, corresponding to loss of one ethanol molecule is quite close to the theoretically calculated value (10.8%). The relevant DTA curve shows an endothermic peaks at 178°C. Two other weight losses are observed and have endothermic peak at 295 and 462°C, respectively; the first mass loss occurs between 260 and 409°C, and is probably due to partial decomposition of the ligand. The secod mass loss, in the range 434–506°C, is assigned to the complete decomposition of the ligand with formation of metal oxides.[20] The final residue comprises 22.0% weight, coinciding with $V_2O_5$ (21.4%). TGA studies demonstrate that the thermal stability of the complex is higher than that of the ligand.

## SUPPLEMENTARY MATERIAL

Atomic coordinates for the hydrogen atoms, thermal parameters, full lists of bondlengths, bond angles, torsion angles and observed and calculated structure factors for the complex are available from the authors on request.

### *References*

1. N.D. Chasteen, Ed., "Vanadium in Biological Systems," (Kluwer Academic Publishers, Dordrecht, The Netherlands, 1990).
2. D. Rehder, *Angew. Chem. Int. Ed. Engl.*, **30**, 148 (1991).
3. J.J.R. Frausto da Silva, "*Chemical Speciation and Bioavailability,*" **1**, 139 (1989).
4. R. Wever and K. Kustin, *Adv. Inorg. Chem.*, **35**, 103 (1990).
5. N.D. Chasteen, J.K. Grady and C.E. Holloway, *Inorg. Chem.*, **25**, 2754 (1986).
6. V. Vergopoulos, W. Priebsch, M. Fritzsche and D. Rehder, *Inorg. Chem.*, **32**, 1844 (1993).
7. D.C. Crans, R.L. Bunch and L.A. Theisen, *J. Amer. Chem. Soc.*, **111**, 7597 (1989).
8. E. de Boer, M.G.M., Tromp, H. Plat, G.E. Krenn and R. Wever, *Biochim. Biophys. Acta,* **872**, 104 (1986).
9. M.J. Clague, N.L. Keder and A. Butler, *Inorg. Chem.*, **32**, 4754 (1993).
10. H.-X. Liu, W. Wang, X. Wang and M.-Y Tan *J. Coord. Chem.*, **33**, 347 (1994).
11. K.F. Jahr, J. Fuchs and O. Oberhauser, *Chem. ber.*, **101**, 482 (1968).
12. B.A. Frenz, The Enraf-Nonius CAD4 SDP, A real-time System for Concurrent X-Ray Data Collection and Crystal Structure Determination, In "*Computing in Crystallography,*" Eds. H. Schenk, R. Olthaf-Hazekamp, H. Vankoningsveld and G.C. Bassi, (Delft University Press, Delft, 1978), p. 64.
13. J.C. Dutton, G.D. Fallon and K.S. Murray, *Inorg. Chem.*, **27**, 34 (1988).
14. C.J. Carrano, C.M. Nunn, R. Quan, J.A. Bonadies and V.L. Pecoraro, *Inorg. Chem.*, **29**, 944 (1990).
15. K. Nakajima, M. Kojima, K. Toriumi, K. Saito and J. Fujita, *Bull. Chem. Soc. Jpn.*, **62**, 760 (1989).
16. U. Casellato, P.A. Vigato, R. Graziani, M. Vidali, F. Milani and M.M. Muisiani, *Inorg. Chim. Acta,* **61**, 121 (1982).'
17. X. Wang, X.-M. Zhang and H.-X. Liu, *Inorg. Chim. Acta,* **223**, 193 (1994).
18. J. Selbin, *J. Chem. Educ.*, **41**, 86 (1964).
19. C.G. Barraclough, J. Lewis and R.S. Nyholm, *J. Chem. Soc.*, 3552 (1954).
20. H.L. David, M. Ionashiro, A.V. Benedetti, J.R. Zamian and E.R. Dockal, *Thermochimica Acta,* **202**, 45 (1992).