

Structural Aspects and Spectroscopic Characterization of a Mn(II) Complex with Unsymmetrical NNO-Donor Hydrazone Ligand

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Abstract The manganese(II) complex, $\text{Mn}[\text{C}_5\text{H}_4\text{N}-\text{C}(\text{CH}_3)=\text{N}-\text{N}=\text{C}(\text{O})-\text{C}_6\text{H}_5]_2$ (**1**) containing *N,N,O*-donor hydrazone ligand is characterized by X-ray diffraction study. The ligand is the 1:1 condensation product of benzhydrazide and 2-acetylpyridine. The spectral, cyclic voltammetric and room-temperature magnetic moment data are used to establish structure and electronic structure of the compound. Structural investigation shows that **1** crystallizes to a monoclinic system, space group C2/c , $a = 22.8367(13)$, $b = 10.1523(6)$, $c = 12.0736(7)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 116.5930(10)^\circ$, and $Z = 4$. The central manganese atom is in an N_4O_2 coordination sphere constituted by the NNO donor sets of the two independently hydrazone ligands. The Mn–N1, Mn–N2 and Mn–O1 bond distances are 2.3255(15), 2.1854(13) and 2.1361(13) Å, respectively. The effective magnetic moment (μ_{eff}) value of **1** is found to be 5.92 B.M. at 300 K. Cyclic voltammetry shows Mn(III)/Mn(II) couple at 0.9 V and imine reductions at –0.68 and at –1.3 V.

Keywords Manganese(II) complex · Hydrazone · Spectral properties · Crystal structure

Introduction

Hydrazone ligands have similarities in their donor properties with unsymmetrical salen (condensation product of salicylaldehyde and 1,2-diaminoethane) type ligands. Recently it was reported that such ligands, like non-symmetrical salen, can act as effective catalysts towards alkene epoxidation [1]. Hydrazones belong to azomethine function and have been characterized by tri-atomic grouping $\text{C}=\text{N}-\text{N}$ and they are interesting substances because some of them play an important role in the treatment of several diseases, such as tuberculosis. Such an activity is directly attributed to the formation of stable chelates with transition metals that catalyze the corresponding physiological processes [2]. In analytical chemistry also, hydrazone ligands find wide applications as transition metal binders [3, 4]. Studies have also shown that the azomethine–N, which has a lone pair of electrons in a sp^2 hybridized orbital, has considerable biological importance [5]. Arylhydrazone complexes of transition metal ions are known to provide useful models for elucidation of the mechanism of enzyme inhibition [6] and for their possible pharmacological applications [7]. Additionally, hydrazone complexes have been the subject of studies over many years for their antimicrobial and anti-tumor activities [8–14]. Hydrazone ligands can coordinate in neutral [15], monoanionic [16], dianionic [17, 18] or tetraanionic [19] forms, to the metal ions which have coordination numbers of six and seven [20]; generating mononuclear or binuclear species. Some benzoylhydrazone complexes of copper [21], vanadium [22, 23], ruthenium [24] and manganese [25] have been discussed previously. In the present contribution, we describe the synthesis of a mononuclear manganese(II) complex, $\text{Mn}[\text{C}_5\text{H}_4\text{N}-\text{C}(\text{CH}_3)=\text{N}-\text{N}=\text{C}(\text{O})-\text{C}_6\text{H}_5]_2$ (**1**) using a hydrazone ligand, (Hacpbh) [26–28]. We characterize the complex

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by single crystal X-ray diffraction study as well as the elemental analyses, IR and UV–Vis spectra, cyclic voltammetry and room-temperature magnetic measurements. By means of X-ray diffraction study it shows that the manganese ion is in N_4O_2 environment coordination via pyridine–N, imine–N and deprotonated amide–O of the two sets of hydrazone ligands.

Experimental

Materials

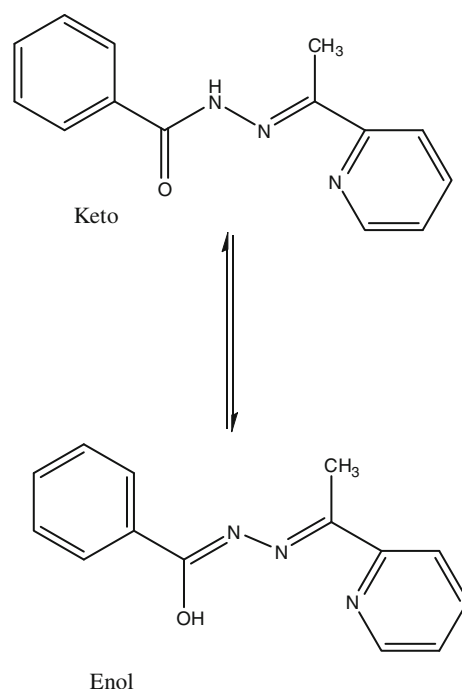
All chemicals and solvents used for the synthesis were of reagent grade. Benzhydrazide (Fluka), 2-acetylpyridine and manganese chloride tetrahydrate (Aldrich Chemicals Co) were obtained commercially and used without purification.

Physical Techniques

C, H, N analysis was carried out using a Perkin-Elmer 240C elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer 883-Infrared spectrophotometer in the range $4,000\text{--}200\text{ cm}^{-1}$ as KBr pellets. The electronic spectra were recorded at 300 K on a Perkin-Elmer λ -40 UV/Vis spectrometer using HPLC grade acetonitrile as solvent with a 1 cm quartz cuvettes in the range 200–800 nm. Magnetic susceptibility was measured on a powder sample in a vibrating sample magnetometer using mercury(tetrathiocyanato)cobaltate as the standard. Thermal analysis was carried out at a heating rate of $10\text{ }^\circ\text{C/min}$ with a Mettler-Toledo Star TGA/SDTA-851e thermal analyzer system in a dynamic atmosphere of N_2 (flow rate 30 mL/min) in an alumina crucible for the range $25\text{--}375\text{ }^\circ\text{C}$. Electrochemical studies were carried out with a CH 600A cyclic voltammeter instrument using acetonitrile as solvent and 0.1(M) tetrabutylammonium perchlorate as the supporting electrolyte using Pt-disk milli working, Pt-wire auxiliary and SCE reference electrodes under dry N_2 environment.

Preparation of the Ligand, $C_5H_4N\text{--}C(CH_3)=N\text{--}N=C(OH)\text{--}C_6H_5$ (Hacpbh)

The ligand, Hacpbh was prepared by the condensation of benzhydrazide (1.36 g, 10 mmol) and 2-acetylpyridine (1.12 mL, 10 mmol) in 50 mL of methanol according to the procedure reported elsewhere [29]. The resulting yellow solution containing the tridentate Schiff base was used without further purification. The ligand exhibits a keto–enol tautomerism (Scheme 1) and can coordinate in monoanionic form to the metal center.



Scheme 1 Keto-enol tautomerism of the hydrazone ligand

Preparation of the Complex $Mn[C_5H_4N\text{--}C(CH_3)=N\text{--}N=C(O)\text{--}C_6H_5]_2$ (**1**)

To methanol solution of Hacpbh (2 mmol), $MnCl_2\cdot 4H_2O$ (0.197 g, 1 mmol) in a minimum amount of water was added and stirred for 1 h. Then the resulting mixture was kept at room temperature without any disturbance. After a few days brown crystals of **1** were formed on slow evaporation of the solvent and collected the crystals suitable for X-ray diffraction. Yield. (65%). Anal. Calc. for $C_{28}H_{24}MnN_6O_2$: C 63.28, H 4.55, N 15.81. Found: C 63.17, H 4.62, N 5.68%.

X-Ray Crystallography

Details concerning crystal data, data collection characteristics and structure refinement are summarized in Table 1. Diffraction data were measured at 150(2) K on a Bruker AXS P4 four-circle diffractometer fitted with graphite-monochromated Mo- K_α ($\lambda = 0.71073\text{ \AA}$) and the $\omega:2\theta$ scan technique for data collection within a θ range of $1.99\text{--}26.01^\circ$. The crystal was mounted on a fiber with epoxy and a total of 6934 reflections were collected from which 2,474 independent [$R(\text{int}) = 0.0236$] reflections were measured. The structure was solved by direct methods using the SHELXTL PLUS [30] system and refined by a full-matrix least-squares methods based on F^2 using SHELXL93 [31] using all 6,934 data to final wR_2 (on F^2 , all data) = 0.0981 and R_1 [on F , with ($I > 2\sigma(I)$) = 0.0347.

Table 1 Crystallographic data for **1**

Empirical formula	C ₂₈ H ₂₄ N ₆ MnO ₂
Formula weight	531.47
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 22.8367(13)$ Å, $\alpha = 90^\circ$ $b = 10.1523(6)$ Å, $\beta = 116.5930(10)^\circ$ $c = 12.0736(7)$ Å, $\gamma = 90^\circ$
Volume	$2503.1(3)$ Å ³
Z	4
Density (calculated)	1.410 Mg/m ³
Absorption coefficient	0.566 mm ⁻¹
$F(000)$	1,100
Crystal size	$0.37 \times 0.25 \times 0.21$ mm ³
Theta range for data collection	$1.99\text{--}26.01^\circ$
Reflections collected	6,934
Independent reflections	2,474 [$R(\text{int}) = 0.0236$]
Max. and min. transmission	0.8905 and 0.8180
Data/restraints/parameters	2474/0/169
Goodness-of-fit on F^2	1.059
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0347$, $wR2 = 0.0944$
R indices (all data)	$R1 = 0.0385$, $wR2 = 0.0981$
Largest diff. peak and hole	0.287 and -0.444 e Å ⁻³

The functions minimized were $\sum w[|F_o|^2 - |F_c|^2]^2$, where $w = [\sigma^2(I) + (0.0849P)^2 + 0.3606P]^{-1}$ for **1** with $P = (|F_o|^2 + 2|F_c|^2)/3$. In this case, non-hydrogen atoms were refined employing anisotropic displacement parameters and the hydrogen atom positions were calculated with fixed isotropic displacement parameters. The crystallographic data and refinement results are listed in Table 1.

Results and Discussion

The ligand, [C₅H₄N–C(CH₃)=N–N=C(OH)–C₆H₅] (Hacpbh), synthesized by the condensation of benzhydrazide with 2-acetylpyridine, exhibits a keto–enol tautomerism (Scheme 1) and can coordinate in monoanionic form to the metal center.

Infrared Spectra

The IR spectrum of **1** has been recorded in the region 4,000–250 cm⁻¹ and the stretching vibrations are fully consistent with the functional groups observed in the X-ray structure of the compound. The IR spectrum of the hydrazone ligand contains a strong C–O absorption band at

1,654 cm⁻¹ and $\nu(\text{N–H})$ at 3,225 cm⁻¹. Both of these bands disappear on complexation, and a new C–O absorption band appears at 1,060 cm⁻¹ in **1**, indicating that the hydrazone ligand has undergone deprotonation on complexation and coordinates in enol form. These data give evidence for the coordination of the deprotonated ligand, acpbh^- (C₅H₄N–C(CH₃)=N–N=C(O)–C₆H₅) to the Mn(II) ion via two nitrogen atoms and one oxygen atom. The infrared spectrum of **1** displays IR stretching at 1,581 cm⁻¹ which can be assigned to the $\nu_{(\text{C}=\text{N})}$ of the coordinated ligand (acpbh^-) [32], whereas for the free ligand (Hacpbh) the same band is observed at 1,681 cm⁻¹. The shift of this band on complexation towards lower frequency indicates coordination of the azomethane nitrogen to the metal centre [33]. Coordination of the ligand is further substantiated by the frequencies at 414 and 365 cm⁻¹, assignable to $\nu_{(\text{Mn–N})}$ and $\nu_{(\text{Mn–O})}$ stretching frequencies, respectively. The low energy pyridine ring in plane and out of plane vibrations are observed in the spectrum of the free ligand at 635 and 409 cm⁻¹ respectively whereas the corresponding band for the complex has been shifted to higher frequencies at 680–715 and 421–426 cm⁻¹, which is a good indication of the coordination of the heterocyclic nitrogen [34]. These data give evidence for the coordination of the ligand (Hacpbh) to the Mn(II) ion via two nitrogen atoms and one oxygen atom.

Electronic Spectra

A UV–Vis spectrum of **1** was recorded at 300 K in HPLC grade acetonitrile solution. We obtained two bands in the UV region considering the distorted octahedral geometry of Mn(II) ion. The band obtained at 376 nm is considerably stronger than the band obtained at 248 nm. According to literature these bands are mainly assigned due to $n \rightarrow \pi^*$ (forbidden transition) and $\pi \rightarrow \pi^*$ transition in the ligand. It is well known that the $d-d$ transition in d^5 system is spin forbidden and transitions are of very low intensities, and hence, in **1** we did not observe any $d-d$ bands for such transitions [35].

Magnetic Study

The Mn(II) complex, **1** exhibits room temperature magnetic susceptibility as expected for isolated d^5 transition metal centers. The effective magnetic moment (μ_{eff}) value is found to be 5.92 B.M. at 300 K. The value is consistent with the magnetically dilute high spin d^5 Mn(II) complex [36].

Thermal Analysis

The thermal decomposition trace of **1** has been recorded. The TGA experiment of **1** indicates that it is stable up to $\sim 295^\circ\text{C}$ and then begins to lose the Schiff base in the

temperature range, 305–370 °C. There are no intermediates and hence the total mass loss corresponds to one equivalent of Schiff base.

Crystal Structure

Figure 1 shows a perspective drawing of the molecule **1** together with the selective atom labeling and the necessary bond distances and angles are shown in Table 2. The Mn(II) ion possesses in N_4O_2 coordination sphere. Each of the two meridionally spanning ligands ($acpbh^-$) coordinates the metal ion via the pyridine-N, imine-N and deprotonated amide-O atoms with an ‘interligand angle’ (dihedral angle) of $84.61(3)^\circ$ and formed two five member chelate rings. The average N–N (1.377 Å), N–C (1.333 Å) and C–O (1.269 Å) distances in the $[=N-N=C(O^-)]$ moiety of both ligands conform with the enolate form of the amide functionalities and charge delocalization over the

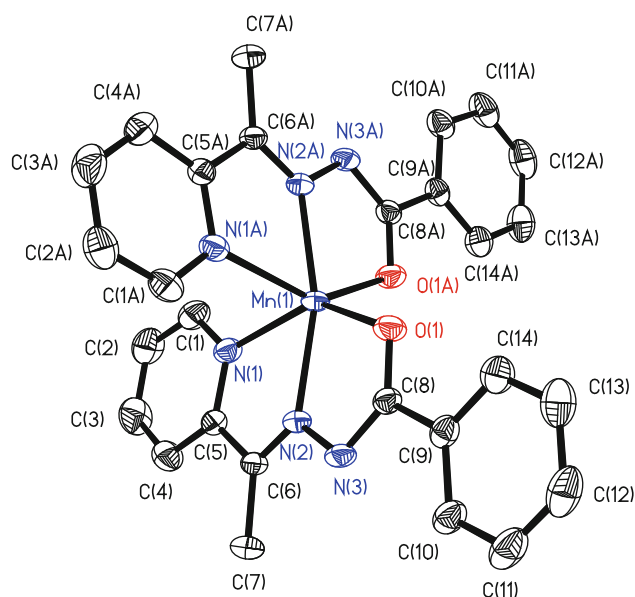


Fig. 1 An ORTEP plot of complex **1**. Ellipsoids are drawn from 40% probability label. Hydrogen atoms have been omitted for clarity

Table 2 Selected bond lengths [Å] and angles [$^\circ$] for **1**

Mn1–N1	2.3255(15)	Mn1–N2	2.1854(13)
Mn1–O1	2.1361(13)	Mn1–O1#1	2.1361(13)
Mn1–N1#1	2.3255(15)	Mn1–N2#1	2.1854(13)
C6–N2	1.289(2)	N2–N3	1.377(2)
N3–C8	1.333(2)	C8–O1	1.269(2)
Mn1–O1–C8	114.66(11)	O1–C8–N3	126.37(15)
C8–N3–N2	109.02(13)	N3–N2–Mn1	117.62(10)
N2–Mn1–O1	72.29(5)	N1–Mn1–N2	70.49(5)
Mn1–N2–C6	123.46(11)	N2–C6–C5	114.41(14)
C6–C5–N1	116.21(14)	C5–N1–Mn1	115.17(11)

chelating fragment. A large distortion of the MnN_4O_2 octahedron is clearly evident from the bond distances and angles given in Table 2. One characteristic feature of the structure is that the two $acpbh^-$ moieties are equivalent with respect to the metal to coordinating atom distances. The manganese and imine nitrogen (Mn1–N2) separation is 2.1854(13) Å. The Mn(II) pyridine–N and Mn(II) amide–O distances for the chelating ligand are significantly different. The distance between Mn1–N1 and Mn1–O1 are 2.3255(15) and 2.1361(13) Å, respectively. The Mn–N (pyridine), Mn–N (imine) and Mn–O bond distances [2.3255(15), 2.1854(13) and 2.1361(13) Å] are comparable to the previously reported Mn–N and Mn–O distances [2.218(3), 2.241(3) and 2.170(3) Å] [37] and other previous literatures, like M–N (pyridine), M–N (imine) and M–O distances, [M=Cu, 2.012(3), 1.928(3) and 1.965(3) Å] [26], [M=Cd, 2.4135(11), 2.2666(11) and 2.2685 Å] [27], [M=Cu, 2.020(5), 1.924(4) and 1.959(4) Å] [28]. There is also an indication of angular distortions in the octahedron which are caused by the different bite angles in the adjacent five-member chelate rings, Mn1–O1–C8, O1–C8–N3, C8–N3–N2, N3–N2–Mn1 and N2–Mn1–O1 i.e., $114.66(11)$, $126.37(15)$, $109.02(13)$, $117.62(10)$ and $72.29(5)^\circ$, respectively and Mn1–N2–C6, N2–C6–C5, C6–C5–N1, C5–N1–Mn1, N1–Mn1–N2, i.e., $123.46(11)$, $114.41(14)$, $116.21(14)$, $115.17(11)$, $70.49(5)^\circ$, respectively and vice versa in consideration the other $acpbh^-$ ligand. The hydrazone ligands of N(3) are linked in chains, as in compound **1**, by the overlap of nearly parallel, neighbouring C(9–14) and C(1–5) rings.

Redox Study

Cyclic voltammogram of the complex is recorded in MeCN at a Pt-disk milli electrode in the potential range +1.6 to –2.0 V versus SCE reference electrode (Fig. 2). Voltammogram shows an oxidative response at 0.9 V with a weak

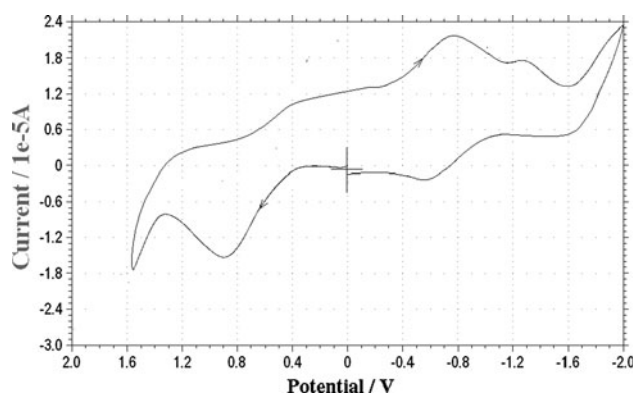


Fig. 2 Cyclic voltammogram of the complex in MeCN using Pt-disk working electrode, Pt-wire auxiliary and SCE reference electrode in presence of $[n-Bu_4N](ClO_4)$ supporting electrolyte at 50 mV S^{-1} scan rate at 300 K

reductive response at 0.4 V. On scanning to negative direction up to -2.0 V we observe one quasireversible reduction at -0.68 V (peak-to-peak separation, ΔE_p , 190 mV) and a second irreversible reduction at -1.3 V. The oxidation may refer to electron extraction from metal ion and is assigned to Mn(III)/Mn(II) redox response. The free ligand is π -acidic keto or enol tautomer type system while in the complex it is enolato function and may have several reductive forms. So the reduction at -0.68 V may be assigned to imine reduction $(-C=N-)/(-C=N-)^-$. The reduction at more negative potential (-1.3 V) may be raised from the repulsion of second electron addition to already reduced motif.

Conclusion

In this paper, we have reported one new octahedral Mn(II) complex with a hydrazone ligand (Hacpbh) having NNO donor sets. The complex has been characterized by analytical, spectral and magnetic methods. Redox activity of the complex shows Mn(III)/Mn(II) response along with imine reductions. Structural characterizations by single-crystal X-ray diffraction analysis has also been discussed and the central Mn(II) ion possesses a distorted octahedral geometry. Our next attempt will be to focus on the synthesis of different hydrazone ligands incorporating substituents on the phenyl ring and investigating the coordination modes of other transition metal complexes.

Supplementary Material

Crystallographic data has been deposited at the Cambridge Crystallographic Data Center with deposition number 725518. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1233-336033; E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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References

- Pouralimardan O, Chamayou AC, Janiak C, Monfared HH (2007) *Inorg Chim Acta* 360:1599
- Geubeur I, Guekezian M, Terra LHSA, Moraes MCB, Lago CL, Matos JR, Suárez-Iha ME (2004) *Polyhedron* 23:2095
- Suez IHA, Pehkonen SO, Hoffmann MR (1994) *Sci Technol* 28:2080
- Terra LH, Areias AMC, Gaubeur I, Suez-Iha MEV (1999) *Spectrosc Lett* 32:257
- Patai S (1970) *The chemistry of carbon–nitrogen double bond*. Interscience, New York
- Iskander MF, Zayan SE, Khalifa MA, Elsayed L (1974) *J Inorg Nucl Chem* 36:556
- Marchent JR, Clothia DS (1970) *J Med Chem* 13:335
- Sridhar S, Saravanan M, Ramesh A (2001) *Eur J Med Chem* 36:615
- Bottari B, Maccari R, Monforte F, Ottana R, Rotondo E, Vigorita M (2000) *Bioorg Med Chem Lett* 10:657
- Kaymakciogul B, Rollas S (2002) *Farmaco* 57:595
- Ainscough E, Brodie A, Ranford J, Waters M (1995) *Inorg Chim Acta* 236:83
- Ainscough E, Brodie A, Ranford J, Waters M (1998) *Inorg Chim Acta* 267:27
- Easmon J, Puerstinger G, Roth T, Feibig H, Jenny M, Jaeger W, Heinisch G, Hofmann J (2001) *Int J Cancer* 94:89
- Küçükgül S, Rollas S, Küçükgül I, Kiraz M (1999) *Eur J Med Chem* 34:1093
- Seth S, Chakraborty S (1984) *Acta Crystallogr C* 40:1530
- de Sousa GF, Filgueiras CAL, Abras A, Al-Juaied SS, Hitchcock PB, Nixon JF (1994) *Inorg Chim Acta* 218:139
- Andjelković K, Ivanović I, Niketić SR, Prelesnik B, Leovac VM (1997) *Polyhedron* 16:4221
- And-jelković K, Jakovljević G, Zlatović M, Tešić Ž, Sladić D, Howing J, Tellgren R (2004) *J Serb Chem Soc* 69:651
- Bonardi A, Merlo C, Pelizzi C, Pelizzi G, Tarasconi P, Vitali F, Cavatorta F (1991) *J Chem Soc Dalton Trans* 1063
- Palenik GJ, Wester DW (1978) *Inorg Chem* 17:864
- Sangeetha NR, Pal S, Pal S (2000) *Polyhedron* 19:2713
- Plass W, Pohlmann A, Yozgatli HP (2000) *J Inorg Biochem* 80:181
- Dinda R, Sengupta P, Ghosh S, Mak TCW (2002) *Inorg Chem* 41:1684
- Raveendran R, Pal S (2005) *Polyhedron* 24:57
- Naskar S, Biswas S, Mishra D, Adhikary B, Falvello LR, Soler T, Schwalbe CH, Chattopadhyay SK (2004) *Inorg Chim Acta* 357:4257
- Sen S, Mitra S, Hughes DL, Rosair G, Desplanches C (2007) *Polyhedron* 26:1740
- Sen S, Talukder P, Rosair G, Mitra S (2005) *Struct Chem* 16:605
- Sen S, Mitra S, Hughes DL, Rosair G, Desplanches C (2007) *Inorg Chim Acta* 360:4085
- Khalil TE, Labib L, Iskander MF (1994) *Polyhedron* 13:2569
- Sheldrick GM (1990) *SHELXL-PLUS*. Siemens X-ray Analytical Instruments Inc., Madison
- Sheldrick GM (1993) *SHELXL 93: program for crystal structure refinement*. University of Göttingen, Germany
- Addison AW, Rao TN, Reedijk J, van Rijn J, Verschoor GC (1984) *J Chem Soc Dalton Trans* 1349
- Conley RT (1966) *Infrared spectroscopy*. Allyn & Bacon, Boston
- Nakamoto K (1997) *Infrared and Raman spectra of inorganic and coordination compounds, parts A and B*, 5th edn. Wiley, New York
- Lever ABP (1984) *Inorganic electronic spectroscopy*, 2nd edn. Elsevier, Amsterdam
- Batra G, Mathur P (1994) *Trans Met Chem* 19:160
- Sen S, Mitra S, Luneau D, El Fallah MS, Ribas J (2006) *Polyhedron* 25:2737