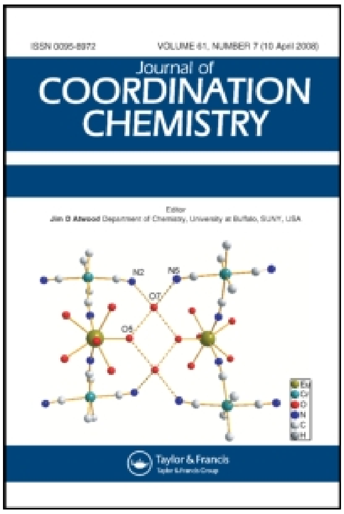


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS, STRUCTURE AND PROPERTIES OF MANGANESE(II) COMPLEXES WITH AROYLHYDRAZONES OF 2-PYRIDINE-CARBOXALDEHYDE

Amitava Choudhury[a]; Banda Geetha[a]; Nimma Rajaiah Sangeetha[a]; Vanaparthi Kavita[a]; Vishnubhatla Susila[a]; Samudranil Pal[a]
[a] School of Chemistry, University of Hyderabad, Hyderabad, India

To cite this Article Choudhury, Amitava , Geetha, Banda , Sangeetha, Nimma Rajaiah , Kavita, Vanaparthi , Susila, Vishnubhatla and Pal, Samudranil(1999) 'SYNTHESIS, STRUCTURE AND PROPERTIES OF MANGANESE(II) COMPLEXES WITH AROYLHYDRAZONES OF 2-PYRIDINE-CARBOXALDEHYDE', Journal of Coordination Chemistry, 48: 1, 87 — 95

To link to this Article: DOI: 10.1080/00958979908024367

URL: http://dx.doi.org/10.1080/00958979908024367

J. Coord. Chem., 1999, Vol. 48, pp. 87–95
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

SYNTHESIS, STRUCTURE AND PROPERTIES OF MANGANESE(II) COMPLEXES WITH AROYLHYDRAZONES OF 2-PYRIDINE-CARBOXALDEHYDE

AMITAVA CHOUDHURY, BANDA GEETHA,
NIMMA RAJAIAH SANGEETHA, VANAPARTHI KAVITA,
VISHNUBHATLA SUSILA and SAMUDRANIL PAL*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

(Received 18 June 1998)

Manganese(II) complexes of terdentate *N,N,O* donor Schiff bases (HL) are described. The ligands Hpabh, Hpamh and Hpadh are obtained by condensing 2-pyridine-carboxaldehyde with benzhydrazide, 4-methoxybenzhydrazide and 4-dimethylaminobenzhydrazide, respectively. The reaction of HL with manganese(II) acetate tetrahydrate affords $[MnL_2]$. The crystal structure determination of $[Mn(pabh)_2]$ was performed. The complex crystallises in the space group $P2_1/n$ with $a = 9.836(3)$, $b = 23.994(7)$, $c = 10.222(3)$ Å, $\beta = 104.14(3)°$, $V = 2339.5(13)$ Å^3 and $Z = 4$. In the distorted octahedral MnN_4O_2 coordination sphere each ligand acts as a meridional *N,N,O* donor utilising pyridine-*N*, imine-*N* and amide-*O* atoms. Electronic spectra of the complexes display charge transfer bands in the range 404–298 nm. Room temperature solid state magnetic moments ($5.88-6.12\mu_B$) of the complexes are consistent with a high-spin d^5 system. EPR spectra of the complexes suggest a similar distorted octahedral N_4O_2 coordination sphere around Mn(II) in each complex.

Keywords: Manganese(II); amide; X-ray structure

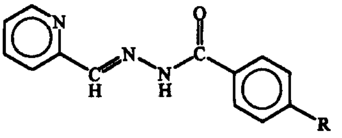
INTRODUCTION

Transition metal complexes of aroylhydrazones provide useful models to elucidate the mechanisms of enzyme inhibition by hydrazine derivatives.[1] These complexes are also important with respect to their pharmacological

---

* Corresponding author.

applications.[2] In this work we have studied the coordination chemistry of manganese(II) using 2-pyridine-carboxaldehyde aroylhydrazones as ligands (I). Each of the three terdentate Schiff base ligands has one dissociable amide proton. The deprotonated monoanionic planar ligand can coordinate a metal ion *via* the pyridine-*N*, imine-*N* and the deprotonated amide-*O* atoms forming two five-membered chelate rings. The synthesis and properties of mononuclear manganese(II) complexes of the above ligands are described. The solid state structure of one of the complexes has been determined by X-ray crystallography.



(I)

Hpabh (R = H)
Hpamh (R = OMe)
Hpadh (R = NMe$_2$)

EXPERIMENTAL

Materials

The chemicals and solvents used in this work were of analytical grade available commercially and were used without further purification.

Physical Measurements

Microanalytical (C, H, N) data were obtained with a Perkin-Elmer Model 240C instrument. Electronic spectra were recorded on a JASCO-7800 spectrophotometer. A JEOL FE-3X spectrometer was used to obtain the EPR spectra. IR spectra were collected using KBr pellets on a JASCO-5300 FT-IR spectrophotometer. Room temperature solid state magnetic susceptibilities were measured using a CAHN-1000 magnetic balance. Diamagnetic corrections calculated from Pascal's constants[3] were used to obtain molar paramagnetic susceptibilities. Solution electrical conductivities were measured with a Digisun DI-909 conductivity meter.

Preparation of Compounds

The ligands were prepared in high yield (75–90%) by condensing one equivalent of 2-pyridine-carboxaldehyde with one equivalent of corresponding aroylhydrazine in methanol. The complexes can be prepared by following either of the two procedures described below.

[Mn(pabh)$_2$]

To a methanol solution (20 cm^3) of Hpabh (185 mg, 0.82 mmol) was added 100 mg (0.41 mmol) of $Mn(O_2CCH_3)_2 \cdot 4H_2O$ and the mixture was refluxed for 2 h. It was then cooled to room temperature and a brown crystalline solid separated. This was collected by filtration, washed with ice-cold methanol and dried under vacuum. Yield was 110 mg (53%). Selected IR bands[4] (cm^{-1}): 1588(s), 1557(m), 1487(s), 1462(s), 1435(m), 1350(s), 1290(m), 1171(m), 1140(m), 1067(s), 918(m), 860(w), 804(w), 720(s), 691(m), 525(w), 444(w). [Mn(pamh)$_2$] and [Mn(padh)$_2$] can be synthesised from $Mn(O_2CCH_3)_2 \cdot 4H_2O$ and the corresponding ligand (in 1 : 2 mole ratio) by following the above procedure in 22 and 9% yield, respectively.

[Mn(padh)$_2$]

To a solution of Hpadh (220 mg, 0.82 mmol) and KOH (46 mg, 0.82 mmol) in methanol (10 cm^3) was added 5 cm^3 of a methanol solution of 100 mg (0.41 mmol) of $Mn(O_2CCH_3)_2 \cdot 4H_2O$ and the mixture was heated to reflux for 3 h. A dark brown microcrystalline solid separated when the mixture was cooled to room temperature. The complex was collected by filtration, washed with ice-cold water and dried under vacuum over anhydrous $CaCl_2$. Yield was 130 mg (54%). Selected IR bands[4] (cm^{-1}): 1599(s), 1560(m), 1479(m), 1451(m), 1343(s), 1290(s), 1186(s), 1144(w), 1103(w), 1065(s), 945(w), 824(m), 764(s), 700(w), 675(w), 604(m), 507(w). [Mn(pabh)$_2$] and [Mn(pamh)$_2$] can be synthesised by using the above procedure in 69% and 52% yield, respectively. Selected IR bands[4] (cm^{-1}) for [Mn(pamh)$_2$]: 1601(s), 1559(m), 1512(m), 1481(s), 1451(s), 1410(m), 1352(s), 1250(s), 1165(s), 1063(s), 918(m), 843(m), 766(s), 677(m), 617(m), 509(w).

X-ray Structure Determination

Single crystals of [Mn(pabh)$_2$] were grown by slow evaporation of a methanol–toluene (1 : 1) solution of the complex. A crystal of dimension 0.23 × 0.31 × 0.44 mm was used for the data collection on an Enraf-Nonius Mach 3 single crystal diffractometer using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by the least-squares fit of 25 reflections having 2θ values in the range 10–16°. Stability

TABLE I Crystallographic data for [Mn(pabh)$_2$]

Empirical formula	$C_{26}H_{20}N_6O_2Mn$
Formula weight	503.42
Temperature (K)	293
Space group	$P2_1/n$
a(Å)	9.836(3)
b(Å)	23.994(7)
c(Å)	10.222(3)
β(°)	104.14(3)
V(Å^3)	2339.5(13)
Z	4
ρ_{calc}(g cm^{-3})	1.429
μ(mm^{-1})	0.601
F(000)	1036
Data/restraints/parameters	1041/0/186
$R1$[a]	0.0623
$wR2$[b]	0.1437
Goodness-of-fit[c]	1.021

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] Goodness-of-fit $= \{\Sigma[w(F_o^2-F_c^2)^2]/(N_{observn}-N_{parameters})\}^{1/2}$; $w = 1/[\sigma^2F_o^2)+(0.0751P)^2]$, where $P = [2F_c^2+\max(F_o^2,0)]/3$.

of the crystal was monitored by measuring the intensities of two check reflections after every 1.5 h. No decay was observed in the 57 h of exposure to X-rays. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Out of 3371 reflections collected, 3030 are unique and 1041 are observed ($I > 2\sigma(I)$). The complex crystallises in the monoclinic system. The structure was solved in space group $P2_1/n$ by direct methods and refined by full-matrix least-squares on F^2 and Fourier techniques. The asymmetric unit contains a molecule of [Mn(pabh)$_2$]. Due to the limited number of observed data only manganese, oxygen and nitrogen atoms were refined anisotropically. Hydrogen atoms were included at idealised positions for structure factor calculations, but not refined. All calculations were done using the programs of Xtal software[5] for data reduction and SHELX-97 programs[6] for structure solution and refinement. Significant crystal data are summarised in Table I. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table II.

RESULTS AND DISCUSSION

Synthesis and some Properties

Upon reacting one equivalent of acetate salt of bivalent metal ion and two equivalents of the ligand in methanol, the manganese(II) complexes of general formula MnL_2 (L = pabh$^-$, pamh$^-$ and padh$^-$) were obtained. In the

TABLE II Atomic coordinates ($\times 10^4$) and equivalent[a] isotropic displacement coefficients ($Å^2 \times 10^3$) for $[Mn(pabh)_2]$

Atom	x/a	y/b	z/c	U_{ea}
Mn	1436(2)	8938(1)	8929(2)	49(1)
O(1)	3014(7)	8652(3)	10615(7)	56(2)
O(2)	−472(7)	8534(3)	9117(7)	60(2)
N(1)	220(8)	9722(4)	8030(9)	52(2)
N(2)	2450(7)	9666(4)	10030(8)	45(2)
N(3)	3640(8)	9565(3)	11027(8)	45(2)
N(4)	3067(8)	8954(3)	7572(8)	43(2)
N(5)	777(9)	8356(3)	7265(8)	44(2)
N(6)	−464(8)	8075(3)	7143(9)	50(2)
C(1)	−909(11)	9757(5)	7021(11)	61(3)
C(2)	−1565(12)	10255(5)	6572(11)	60(3)
C(3)	−1057(11)	10744(5)	7191(11)	61(3)
C(4)	117(11)	10711(5)	8207(11)	53(3)
C(5)	733(11)	10213(4)	8616(10)	43(3)
C(6)	1989(11)	10156(5)	9725(10)	50(3)
C(7)	3850(10)	9030(4)	11218(10)	47(3)
C(8)	5142(10)	8854(4)	12193(10)	40(2)
C(9)	6205(11)	9241(5)	12747(10)	58(3)
C(10)	7434(12)	9058(5)	13668(11)	60(3)
C(11)	7553(11)	8516(4)	14045(11)	56(3)
C(12)	6535(12)	8144(5)	13525(11)	71(3)
C(13)	5334(11)	8311(4)	12587(10)	52(3)
C(14)	4267(12)	9272(5)	7770(12)	64(3)
C(15)	5130(13)	9243(5)	6912(12)	70(4)
C(16)	4813(12)	8892(5)	5853(12)	67(3)
C(17)	3632(11)	8559(5)	5629(11)	56(3)
C(18)	2750(10)	8615(4)	6527(10)	45(3)
C(19)	1497(11)	8292(5)	6357(12)	57(3)
C(20)	−1021(10)	8217(4)	8167(11)	42(3)
C(21)	−2400(10)	7946(4)	8115(10)	40(2)
C(22)	−3127(11)	8104(5)	9054(11)	64(3)
C(23)	−4456(12)	7882(4)	8965(11)	62(3)
C(24)	−5027(12)	7512(5)	7973(11)	65(3)
C(25)	−4334(11)	7347(5)	7033(11)	63(3)
C(26)	−2990(11)	7573(4)	7120(11)	61(3)

[a] Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

deprotonation of the amide function the acetate of the metal salt acts as the base. However, the yield of the complexes decreases in the order $[Mn(pabh)_2] > [Mn(pamh)_2] > [Mn(padh)_2]$. The acidity of the amide function decreases with the increasing electron donating character of the substituent on the aroyl moiety. Thus the use of a stronger base (OH^-) improves the yield significantly for all the complexes, in particular for $[Mn(padh)_2]$. Elemental analysis data (Table III) for all the complexes are consistent with *bis* chelates. In chloroform as well as in methanol solutions the complexes are non-conducting. Room temperature magnetic moments of the complexes are conforming with an $S = 5/2$ spin state (Table III).

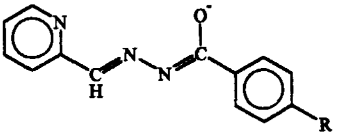
TABLE III Elemental analyses[a] and magnetic susceptibility (298 K) data

Complex	%C	%H	%N	μ_{eff}/μ_B
[Mn(pabh)$_2$]	62.42(62.03)	4.20(4.00)	17.03(16.69)	6.01
[Mn(pamh)$_2$]	61.16(59.68)	4.08(4.29)	15.27(14.91)	6.12
[Mn(padh)$_2$]	61.12(60.79)	5.13(4.86)	19.01(18.84)	5.88

[a]Calculated values are shown in parentheses.

Spectroscopic Properties

The free ligand N–H (~3100 cm^{-1}) and C=O (~1650 cm^{-1}) stretches[7] are not observed in the infrared spectra of the complexes. A strong peak with a shoulder observed at ~1600 cm^{-1} for each of the complexes is possibly due to the conjugate C=N–N=C moiety.[8] The origin of the peak at ~1560 cm^{-1} is most likely to be the C=C stretches from the aromatic part of the ligands.[9] Therefore, in each complex the amide functions of the coordinated ligands exist in the enolate form (II). The monoanionic planar ligand coordinates the metal ion in meridional fashion *via* the pyridine-*N*, imine-*N* and the deprotonated amide-*O* atoms. The X-ray structure (see below) of [Mn(pabh)$_2$] confirms such coordination.



(II)

The electronic spectroscopic profiles of the manganese(II) complexes in methanol solutions are similar. Two strong bands are observed at 363 and 298 nm for [Mn(pabh)$_2$]. The band positions for [Mn(pamh)$_2$] are 369 and 300 nm. On the other hand, [Mn(padh)$_2$] displays a strong absorption at 404 nm followed by a shoulder at 354 nm and another strong absorption at 314 nm. The data are listed in Table IV. The origin of these absorptions is most probably ligand-to-metal charge transfer transitions.[10] There is a low energy shift of the band positions as the substituent on the ligand becomes a better electron donor. Such shifts have been observed for Mn, Fe and Cu complexes.[11]

Frozen solution EPR spectra of the manganese(II) complexes are very similar, indicating a similar N_4O_2 coordination sphere around the Mn(II) centre in all three complexes. In an ideal octahedral symmetry an isotropic signal at $g \sim 2$ is expected. The complexity of the EPR spectrum of a

TABLE IV Electronic[a] and EPR[b,c] spectroscopic data

Complex	λ_{max}/nm(ϵ/$M^{-1}cm^{-1}$)	H/G
[Mn(pabh)$_2$]	363(24000), 298(25500)	1225, 2250, 3125
[Mn(pamh)$_2$]	369(33000), 300(38200)	1325, 2250, 3050
[Mn(padh)$_2$]	404(46500), 354(32300), 314(28800)	1250, 2200, 3100

[a]In CH_3OH. [b]In frozen (150 K) $CHCl_3$. [c]Microwave frequency 9.15 GHz.

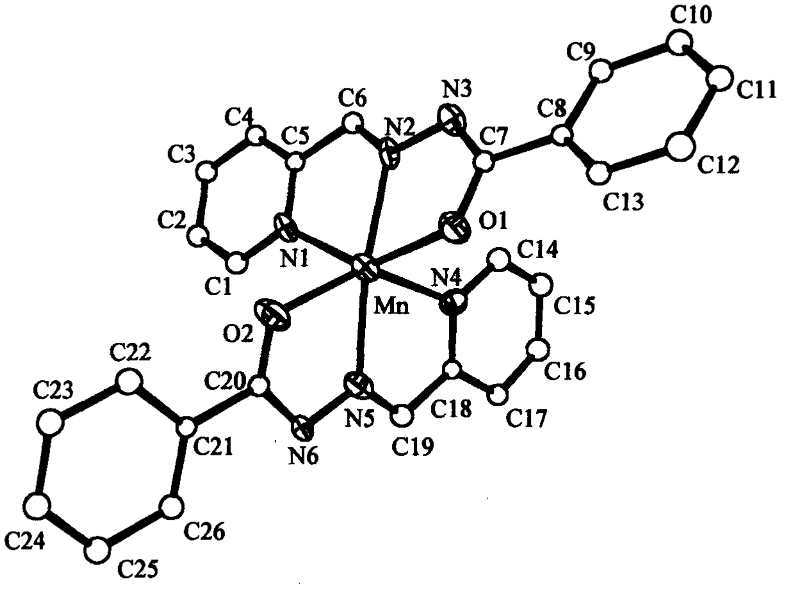


FIGURE 1 Structure of [Mn(pabh)$_2$] showing 30% probability thermal ellipsoids and the atom labelling scheme. Hydrogen atoms are omitted for clarity.

high-spin d^5 system depends upon distortion from octahedral symmetry and the magnitude of zero-field splitting parameters.[12] The present series of complexes display a very broad asymmetric signal centred at ~3100 G preceded by two medium intense resonances at ~1250 and ~2230 G (Table IV). Manganese hyperfine splitting is not resolved in any of the signals. Such spectra are indicative of high zero-field splitting parameters due to distortion of the octahedral symmetry.[13]

Structure of [Mn(pabh)$_2$]

The crystal structure of the complex is shown in Figure 1. Selected bond distances and angles are listed in Table V. The manganese(II) ion has a

TABLE V Selected bond distances (Å) and angles (°) for $[Mn(pabh)_2]$[a]

Bond distances			
Mn–O(1)	2.131(7)	Mn–O(2)	2.161(7)
Mn–N(1)	2.299(9)	Mn–N(2)	2.184(8)
Mn–N(4)	2.364(8)	Mn–N(5)	2.173(8)
Bond angles			
O(1)–Mn–O(2)	105.2(3)	O(1)–Mn–N(1)	142.3(3)
O(1)–Mn–N(2)	71.93(3)	O(1)–Mn–N(4)	90.9(3)
O(1)–Mn–N(5)	116.5(3)	O(2)–Mn–N(1)	91.4(3)
O(2)–Mn–N(2)	127.6(3)	O(2)–Mn–N(4)	142.0(3)
O(2)–Mn–N(5)	71.5(3)	N(1)–Mn–N(2)	71.2(3)
N(1)–Mn–N(4)	96.5(3)	N(1)–Mn–N(5)	100.7(3)
N(2)–Mn–N(4)	89.9(3)	N(2)–Mn–N(5)	158.2(3)
N(4)–Mn–N(5)	70.5(3)		

[a] Numbers in parentheses are estimated standard deviations.

N_4O_2 coordination sphere. Each of the two ligands binds the metal ion meridionally *via* the pyridine-*N*, imine-*N* and deprotonated amide-*O* atoms. The bond distances and angles clearly indicate a large distortion of the MnN_4O_2 octahedron. The chelate bite angles in the five-membered rings formed by the amide-*O* and imine-*N* and the pyridine-*N* and imine-*N* are very similar. The average value is 71.3°. The average N–N (1.373 Å), N–C (1.323 Å) and C–O (1.262 Å) distances of the $=N{-}N{=}C(O^-){-}$ moiety of both the ligands are consistent with the enolate form of the amide functions.[14] The bond distances between the Mn and pyridine-*N* atoms are comparable with distances observed in other structurally characterised Mn(II) complexes having coordinated pyridine-*N*.[15] The Mn–*N* (imine) bond distances are significantly shorter than the Mn–*N* (pyridine) distances. However they are within the range observed for structurally characterised Mn(II) Schiff base complexes.[16] As expected, the bond lengths between Mn(II) and amide-*O* atoms are longer than the metal to amide-*O* distances observed in Mn(III) complexes containing similar ligands.[14a,b]

Acknowledgements

Funding for this work was provided by the Department of Science and Technology, New Delhi. The X-ray structure determination was performed at the National Single Crystal Diffractometer Facility established by the Department of Science and Technology at the School of Chemistry, University of Hyderabad, Hyderabad. Ms N.R. Sangeetha thanks the University Grants Commission, New Delhi for a research fellowship.

Supplementary Material

Listings of anisotropic thermal parameters (Table S1), complete bond distances (Table S2) and angles (Table S3), hydrogen atom positional parameters (Table S4), and observed and calculated structure factors (Table S5) may be obtained from the authors upon request.

References

[1] (a) J.C. Craliz, J.C. Rub, D. Willis and J. Edger, *Nature*, **34**, 176 (1955); (b) M.F. Iskander, S.E. Zayan, M.A. Khalifa and L. El-Sayed, *J. Inorg. Nucl. Chem*., **36**, 556 (1974).

[2] (a) J.R. Merchant and D.S. Clothia, *J. Med. Chem*., **13**, 335 (1970); (b) J.R. Dilworth, *Coord. Chem. Rev*., **21**, 29 (1976).

[3] W.E. Hatfield, *Theory and Applications of Molecular Paramagnetism*, eds. E.A. Boudreaux and L.N. Mulay (John Wiley and Sons, New York, 1976), p. 491.

[4] Symbols: s, strong; m, medium; w, weak.

[5] *Xtal3.4 User's Manual*, eds. S.R. Hall, G.S.D. King and J.M. Stewart (University of Western Australia, Perth, 1995).

[6] G.M. Sheldrick, *SHELX-97 Structure Determination Software* (University of Göttingen, Göttingen, Germany, 1997).

[7] (a) W. Kemp, *Organic Spectroscopy* (Macmillan Education Ltd., Hampshire, 1987), p. 65; (b) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (John Wiley and Sons, New York, 1986), p. 242.

[8] L. El-Sayed and M.F. Iskander, *J. Inorg. Nucl. Chem*., **33**, 435 (1971).

[9] N.S. Biradar and B.R. Havinale, *Inorg. Chim. Acta*, **17**, 435 (1971).

[10] C.J. Carrano, M.W. Carrano, K. Sharma, G. Backes and J. Sanders-Loehr, *Inorg. Chem*., **29**, 101 (1990).

[11] (a) J.W. Pyrz, A.L. Roe, L.J. Stern and L. Que Jr., *J. Am. Chem. Soc*., **107**, 614 (1985); (b) R.N. Mukherjee, O.A. Rajan and A. Chakravorty, *Inorg. Chem*., **21**, 785 (1982); (c) R.J.P. Williams, *J. Chem. Soc*., 137 (1955); (d) N.R. Sangeetha and S. Pal, *J. Coord. Chem*., **42**, 157 (1997); (e) A.V. Lakshmi, N.R. Sangeetha and S. Pal, *Indian J. Chem*., **36A**, 844 (1997).

[12] (a) R.D. Dowsing and J.F. Gibson, *J. Chem. Phys*., **50**, 294 (1969); (b) R.D. Dowsing, J.F. Gibson, M. Goodgame and P.J. Hayward, *J. Chem. Soc. A*, 187 (1969); (c) R. Aasa, *J. Chem. Phys*., **52**, 3919 (1970); (d) D. Collison and A.K. Powell, *Inorg. Chem*., **29**, 4735 (1990).

[13] B. Mabad, P. Cassoux, J.-P. Tuchagues and D.N. Hendrickson, *Inorg. Chem*., **25**, 1420 (1986).

[14] (a) A. Mangia, M. Nardelli, C. Pelizzi and G. Pelizzi, *J. Chem. Soc*., *Dalton Trans*., 1141 (1973); (b) S. Dutta, V. Manivannan, L.G. Babu and S. Pal, *Acta Cryst*., **C51**, 813 (1995); (c) M.R. Maurya, D.C. Antony, S. Gopinathan, V.G. Puranik, S.S. Tavale and C. Gopinathan, *Bull. Chem. Soc. Jpn*., **68**, 2847 (1995); (d) N.R. Sangeetha, C.K. Pal, P. Ghosh and S. Pal, *J. Chem. Soc*., *Dalton Trans*., 3293 (1995); (e) W. Wang, F.-L. Zeng, X. Wang and M.-Y. Tan, *Polyhedron*, **15**, 1699 (1996); (f) X.-M. Zhang, X.-Z. You and X. Wang, *Polyhedron*, **15**, 1793 (1996); (g) S.P. Rath, S. Mondal and A. Chakravorty, *Inorg. Chim. Acta*, **263**, 247 (1997).

[15] H. Oshio, E. Ino, I. Mogi and T. Ito, *Inorg. Chem*., **32**, 5697 (1993).

[16] E. Gallo, E. Solari, S. De Angelis, C. Floriani, N. Re, A. Chiesi-Villa and C. Pizzoli, *J. Am. Chem. Soc*., **115**, 9850 (1993).