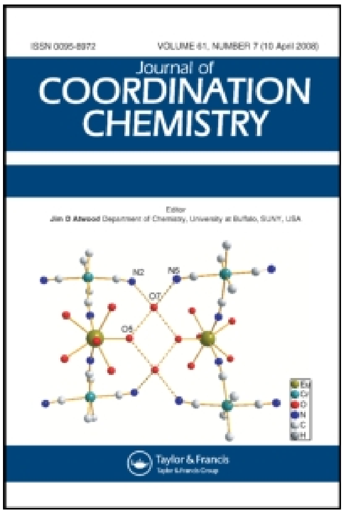


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

MACROCYCLIZATION OF TRANSITION METAL COMPLEXES OF ALPHA-FURILGLYOXIME AND BENZILGLYOXIME

M. Zamil El-faer[a]; Aqil Khan[a]; M. Sakhawat Hussain[a]
[a] Department of Chemistry, University of Petroleum and Minerals, Dhahran, Saudi Arabia

To cite this Article El-faer, M. Zamil , Khan, Aqil and Hussain, M. Sakhawat(1987) 'MACROCYCLIZATION OF TRANSITION METAL COMPLEXES OF ALPHA-FURILGLYOXIME AND BENZILGLYOXIME', Journal of Coordination Chemistry, 16: 1, 81 — 87

To link to this Article: DOI: 10.1080/00958978708079809

URL: http://dx.doi.org/10.1080/00958978708079809

J. Coord. Chem. 1987, Vol. 16 p. 81-87
Photocopying permitted by license only

MACROCYCLIZATION OF TRANSITION METAL COMPLEXES OF ALPHA-FURILGLYOXIME AND BENZILGLYOXIME

M. ZAMIL EL-FAER*, AQIL KHAN and M. SAKHAWAT HUSSAIN*

Department of Chemistry, University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

(Received October 14, 1986; in final form December 19, 1986)

The α-furil- and benzilglyoximates of nickel(II), palladium(II), platinum(II), cobalt(III), rhodium(III) and rhenium(III) have been prepared in a crystalline state and the corresponding macrocycles obtained by reaction with $BF_3 \cdot OEt_2$ utilizing the metal ion as a template. The planar glyoximates yielded macrocycles whereas the macrocyclization of octahedral complexes could not be accomplished. The reactions and the predicted structures have been compared with known structures.

Keywords: glyoximes, complexes, group 8, template, synthesis.

INTRODUCTION

Vicinal glyoximes form inner complexes with several bivalent metal ions through deprotonation followed by interligand hydrogen bond formation.[1] The crystal structures[2-9], infrared spectra[10-14] and magnetic properties[15-19] of several of these complexes have revealed square-planar geometry around the central metal atoms, columnar stacked structures[20] with the adjacent metal atoms engaged in weak metal-metal interactions and a very short O...O distance showing a low-energy infrared band characteristic of strong O--H--O hydrogen bonding.[21] Beside the commonly used ligand dimethylglyoxime [H_2dmg], α-furilglyoxime [H_2afdo] and benzilglyoxime [H_2phdo] have been used as analytical reagents for the determination of trace amounts of metals in various materials. By using metal ions as templates, all of the planar dimethylglyoximates could be converted to macrocycles by substituting hydrogen bridge(s) by the BX_2^+ ($X=F^-$, Cl^- or phenyl), $GaMe_2$ or $InMe_2$ units.[22-24] The BF_2 macrocycles were shown to react with *N*-bases yielding 1:2 adducts. Macrocylization as well as adduct formation reactions are, so far, reported only for the transition metal dimethylglyoximates.

As a part of a continuing research project concerning synthesis by utilizing metal ions as templates, we have carried out the macrocyclization of glyoximates of α-furil- and benzil-glyoximates. Both the macrocyclic compounds as well as their hydrogen bonded precursors were obtained in a crystalline state and have been characterized by spectroscopic procedures. The template effects of the metal ions in these gyloximates to obtain the BF_2-cyclized counterparts are of special interest in the case of cobalt(III), because the chemistry of these complexes resembles that of cobaloximes, which are widely used as chemical models for vitamin B_{12}.

---

*Authors to whom correspondence be directed.

EXPERIMENTAL

Chemicals and Solvents

All chemicals, normal and deuterated solvents were of analytical or spectral grade (Fluka AG) and were used as received except for boron trifluoride etherate which was freshly distilled each time before use.

General Methods of Preparation

The metal glyoximates were obtained in a crystalline state by a modification of procedures used in the spectrophotometric determination of various metal ions.[25–29] The ligands were dissolved in acetone (or ethanol) and added to an aqueous solution of the respective metal salt, keeping metal to ligand ratio 1:2. In most cases a precipitate was formed after pH adjustment and heating of the solution. The residues were separated after digestion. In the case of H_2phdo glyoximates, most of the solvent was evaporated before the solid product was obtained. The residues were washed with ethanol or an acetone-water mixture. Slow evaporation of a dilute solution of the complex in acetone (or chloroform) gave needle-shaped crystals. The macrocyclization was carried out by adding a freshly distilled $BF_3 \cdot OEt_2$ solution to a suspension of the

TABLE I
Analytical results for metal-glyoximates (calculated values in parentheses).

Compound	Colour	Dec. pt (°C)	C (%)	N (%)	H (%)
$[Ni(Hafdo)_2]$	Red	284	48.52 (48.33)	11.28 (11.27)	2.66 (2.82)
$[Ni(BF_2afdo)_2]$	Red	300	39.89 (40.53)	9.06 (9.45)	1.90 (2.04)
$[Pd(Hafdo)_2]$	Orange	155	43.46 (44.10)	10.01 (10.28)	2.41 (3.22)
$[Pd(BF_2afdo)_2]$	Yellow	205	36.90 (37.51)	8.67 (8.74)	1.71 (1.89)
$[Pt(Hafdo)_2]$	Brown	245	36.66 (37.92)	8.82 (8.84)	2.00 (2.23)
$[Pt(BF_2afdo)_2]$	Brown	250	32.01 (32.95)	7.36 (7.68)	1.58 (1.66)
$[Co(Hafdo)_2(H_2O)_2]$	Brown	276	44.08 (45.42)	11.56 (10.51)	2.89 (3.40)
$[Rh(Hafdo)_2]NO_3$	Orange	220	40.11 (39.82)	11.22 (11.61)	2.87 (2.34)
$[Re(Hafdo)_2]Cl$	Violet	150	52.52 (36.4)	12.05 (8.49)	3.42 (2.14)
$[Ni(Hphdo)_2]$	Orange	282	62.57 (62.60)	10.25 (10.43)	4.43 (4.13)
$[Ni(BF_2phdo)_2]$	Yellow	295	53.10 (52.98)	8.87 (8.83)	3.19 (3.18)
$[Pd(Hphdo)_2]$	Orange	182	57.16 (57.50)	9.62 (9.58)	3.74 (3.79)
$[Pd(BF_2phdo)_2]$	Yellow	211	49.60 (49.27)	8.43 (8.20)	2.96 (2.95)
$[Pt(Hphdo)_2]$	Brown	235	49.45 (49.93)	8.15 (8.32)	3.12 (3.29)
$[Pt(BF_2phdo)_2]$	Brown	256	43.54 (43.60)	7.17 (7.26)	2.60 (2.61)
$[Rh(Hphdo)_2]NO_3$	Orange	212	51.71 (52.27)	8.72 (8.71)	4.25 (3.45)

TABLE II
Electronic spectral data for the complexes

Compound	$\lambda_{max}(\alpha_{max} \times 10^{-4})$ (cm^{-1}) $(M^{-1}\ cm^{-1})$	$\lambda_{max}(\alpha_{max} \times 10^{-4})$ (cm^{-1}) $(M^{-1}\ cm^{-1})$
$[Ni(Hafdo)_2]$	37040 (9.74)	22730 (1.29)
$[Pd(Hafdo)_2]$	38460 (6.79)	26320 (0.23)
$[Pt(Hafdo)_2]$	37040 (0.87)	23810 (0.11)
$[Rh(Hafdo)_2]NO_3$	34710 (6.36)	28570 (2.47)
$[Re(Hafdo)_2]Cl$	36760 (65.64)	19610 (10.08)
$[Co(Hafdo)_2(H_2O)_2]$	35710 (5.75)	31650 (5.28)
$[Ni(BF_2afdo)_2]$	37040 (41.01)	22940 (0.36)
$[Pd(BF_2afdo)_2]$	36760 (41.00)	26320 (3.58)
$[Pt(BF_2afdo)_2]$	35090 (3.19)	23810 (1.81)
$[Ni(Hphdo)_2]$	36360 (4.36)	28570 (0.85), 24510 (0.85)
$[Pd(Hphdo)_2]$	38610 (0.93)	3330 (0.44), 22220 (0.41)
$[Pt(Hphdo)_2]$	36360 (0.74)	28570 (0.26), 26320 (0.20)
$[Rh(Hphdo)_2]NO_3$	38460 (3.44)	30300 (0.33)
$[Ni(BF_2phdo)_2]$	38460 (3.98)	25770 (1.34), 24510 (1.33)
$[Pd(BF_2phdo)_2]$	36360 (1.10)	30300 (10.23)
$[Pt(BF_2phdo)_2]$	36630 (0.5)	26320 (0.34)

corresponding uncyclized complex in methylene chloride until the solid (which initially dissolved) changed its colour or a precipitate was formed. The precipitates of the macrocycles were washed with ether, dried under vacuum and crystallized from acetone solution. Elemental analyses were performed on a Carlo Erba 1106 Elemental Analyzer, using vacuum dried complexes. The analytical results are given in Table I.

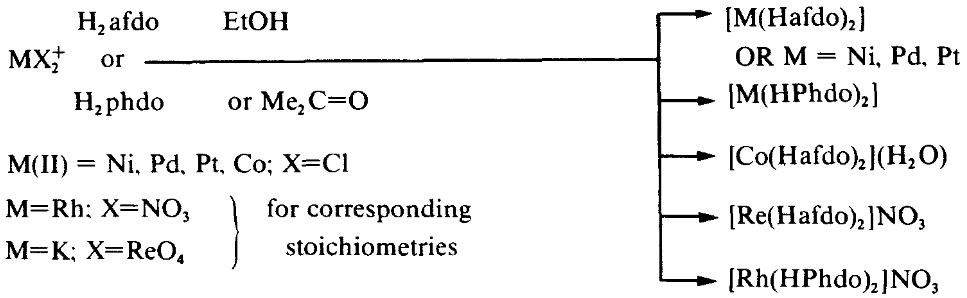
Spectroscopic Measurements

The electronic spectra in the region 200–700 nm were obtained using a Beckman ACTA MVII spectrophotometer. Spectral grade DMSO was used as solvent. The most significant absorption maxima are listed in Table II. Infrared spectra were measured on a Perkin-Elmer 180 spectrophotometer in KBr pellets. All relevant infrared absorption bands and their assignments are listed in Table III. The ^1H nmr spectra were recorded on a Varian T60 or XL200 nmr spectrometer. All solutions were freshly prepared in d_6-DMSO or methylene chloride and TMS was used as internal standard. ^1H nmr chemical shifts for the complexes are listed in Table IV.

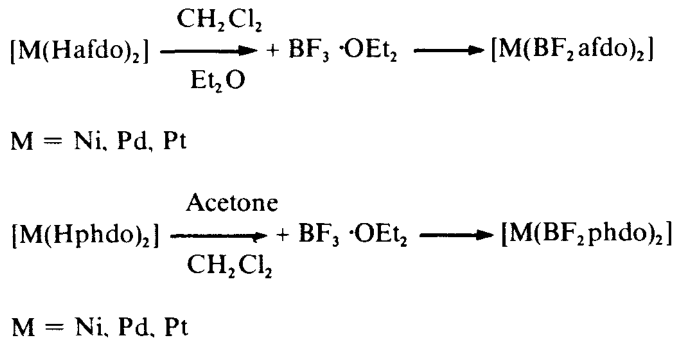
RESULTS AND DISCUSSION

Synthesis

The synthesis pathways for the hydrogen-bonded complexes and the macrocycles are summarized in the Reaction Schemes I and II, respectively. Macrocyclization with BF_2 was possible only for planar glyoximates having a d^8 metal as the template ion. Our efforts to cyclize non-planar Co(II), Re(III) and Rh(III) glyoximates were not successful. Macrocyclization products of $GaMe_2$ or $InMe_2$ were not reported by Kohler *et al.*,[24] for metals other than those having d^8 configuration.



Reaction Scheme I: Synthesis of hydrogen-bonded glyoximates



$$[M(Hafdo)_2] \xrightarrow[Et_2O]{CH_2Cl_2} + BF_3\cdot OEt_2 \longrightarrow [M(BF_2afdo)_2]$$

M = Ni, Pd, Pt

$$[M(Hphdo)_2] \xrightarrow[CH_2Cl_2]{Acetone} + BF_3\cdot OEt_2 \longrightarrow [M(BF_2phdo)_2]$$

M = Ni, Pd, Pt

Reaction Scheme II: Synthesis of Macrocyclic Complexes

Spectroscopic Measurements

Blinc and Hadzi[30] assigned the infrared bands at 2300–2900, 1500–1600 and near 1240 and 1000 cm^{-1} to ν_{OH}, $\nu_{C=N}$ and $\nu_{N\text{-}O}$ in the $[Ni(Hdmg)_2]$, $[Pd(Hdmg)_2]$ and $[Pt(Hdmg)_2]$ complexes. The presence of a strong absorption band around 1700 cm^{-1} and a broad continuum in the region 1000–650 cm^{-1} is considered characteristic of short intramolecular hydrogen bonding, which was confirmed in these glyoximates and for several other complexes by x-ray structure determinations.[31–38] In the macrocycles, Schrauzer and coworkers[22] have assigned the following absorption: $\nu_{B\text{-}F}$ 1026 and 1005 cm^{-1}; $\nu_{N\text{-}O}$ 1200 and 1100 cm^{-1}; $\nu_{B\text{-}O}$ 1193 and 826 cm^{-1}; and $\nu_{C=N}$ 1648 cm^{-1}. In $[Ni(BF_2dmg)_2]$, the high-frequency shift of 68 cm^{-1} in $\nu_{C=N}$ upon encapsulation was explained as a consequence of withdrawal of electron density from the C=N bond by the electronegative BF_2 groups. However in the BF_2-encapsulated H_2afdo macrocycles, the $\nu_{C=N}$ absorption is shifted to lower frequencies by about 40 cm^{-1}. In the H_2afdo complexes, the furan rings neutralize the partial positive charge on the C=N nitrogen atoms (generated by inductive effects of fluorines) through delocalization of the lone pair electron on furan oxygens. This will result in a low

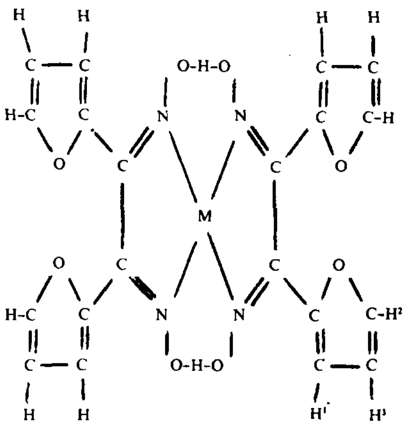
TABLE III
Infrared absorption data (cm^{-1}) for the alpha-furil- and benzilglyoxime complexes (cm^{-1}).

Compound	O-H	O-H-O	C=N	N-O	B-O	B-F
H_2dmg	3205		1490	1212, 1109		
H_2afdo	3200		1550	1234, 1140		
H_2phdo	3200		1450	1220		
$[Ni(Hdmg)_2]$		1260	1500	1212, 1125		
[Ni(Hdmg)		2350	1576	1241, 1103		
$[Ni(BF_2afdo)_2]$			1465	1160, 1120	1210, 880	1040, 930
$[Ni(BF_2dmg)_2]$			1648	1200, 1100	1193, 826	1026, 1005
$[Pd(Hafdo)_2]$		1270	1475	1210, 1110		
$[Pd(BF_2afdo)_2]$			1460	1170, 1120	1225, 870	1070, 980
$[Pt(Hafdo)_2]$		1300	1500	1122, 1220		
$[Pt(BF_2afdo)_2]$			1460	1120	1240, 870	1060, 990
$[Rh(Hafdo)_2]NO_3$	3200		1510	1212, 1130		
$[Co(Hafdo)_2(H_2O)_2]$	3200	1240	1510	1120, 1210		
$[Re(Hafdo)_2]Cl$	3200	1250	1550	1140, 1232		
$[Ni(Hphdo)_2]$		950	1470	1310, 1160		
$[Pd(Hphdo)_2]$		990	1450	1300		
$[Pt(Hphdo)_2]$		1000	1445	1320		
$[Ni(BF_2phdo)_2]$			1470	1240, 1090	1170	1050
$[Pd(BF_2phdo)_2]$			1470	1230	1150	1030
$[Pt(BF_2phdo)_2]$			1460	1320	1230	1020
$[Rh(Hphdo)_2]NO_3$	3200		1460	1250		

TABLE IV
Proton-NMR data (ppm) for alpha-furiglyoximates in d_6-DMSO, and CH_2Cl_2

Compound	$\delta_{O\text{-}H\text{-}O}$	δ_{H1}	δ_{H2}	δ_{H3}
H_2afdo*		8.2	7.2	7.5
H_2afdo	12.9	7.8	6.7	7.5
$[Rh(Hafdo)_2]NO_3$		7.7	6.7	7.4
$[Pt(Hafdo)_2]$		7.7	6.7	7.4
$[Pt(BF_2afdo)_2]$*		6.3		6.1
$[Ni(Hafdo)_2]$	12.2	7.6	6.6	7.6
$[Ni(BF_2afdo)_2]$*		6.3	5.3	6.1
$[Pd(Hafdo)_2]$*		7.6	6.8	7.0
$[Pd(BF_2afdo)_2]$*		6.3	5.2	6.1
$[Re(Hafdo)_2]Cl$	12.8	7.7	6.7	7.5

*O-H-O absorptions were obscured by methylene chloride



energy shift of the C=N absorption. Thus the spectral changes (Table III) for [Pd(Hafdo)$_2$] after treating with $BF_3 \cdot OEt_2$ to form [Pd(BF$_2$afdo$_2$] are a low-energy shift of about 90 cm^{-1} relative to the free ligand in the $\nu_{C=N}$ peak, the appearance of ν_{B-O} absorptions at 870 and 1225 cm^{-1}, and of ν_{B-F} at 980 and 1070 cm^{-1}, the presence of an additional peak at 530 cm^{-1}, the disappearance of the absorption at 1300 cm^{-1} (for the bridged hydrogen) and the shift in the ν_{N-O} absorption from 1235 cm^{-1} in the free ligand to 1170 cm^{-1} in the macrocycle. The band at 1300 cm^{-1} for O-H-O observed in all H$_2$afdo complexes was absent in all macrocycles, as expected. In the case of [Re(Hafdo)$_2$]Cl, a strong band in the 4000-3000 cm^{-1} region indicated uncoordinated -OH but in the complex [Co(Hafdo)$_2$(H$_2$O)$_2$], the peak at 4000-3000 cm^{-1} may be due to coordinated water molecules because the O-H-O continuum is also present in this case. In the Rh(III) complex the bands in 4000-3000 cm^{-1} region were less intense when compared to the free ligand probably due to moisture or the asymmetric nature of the hydrogen bonding. On the basis of the infrared spectra, it is concluded that the intramolecular short hydrogen bonding exists in all cases except in the rhodium(III) and rhenium(III) complexes, complexation is, as usual, through the nitrogen atoms as indicated by the low-energy shifts in the $\nu_{C=N}$ bands and the macrocyclization is possible only for the d^8 complexes, namely [Ni(Hafdo)$_2$], [Pd(Hafdo)$_2$] and [Pt(Hafdo)$_2$].

Proton-NMR Spectra

Different solvents were used for the ^{1}H-n.m.r. spectra because of the low solubility of various complexes in any single solvent. ^{1}H nmr spectra in d$_6$-DMSO showed multiplets centred at 6.6-7.7 ppm for aromatic protons and at 12.0-12.9 ppm for the bridged or hydroxyl protons (Table IV). In methylene chloride, the aromatic protons appeared at 5.2-8.2 ppm whereas the bridged protons were not detected. Even the hydroxyl protons of the ligand, (which were easily detected in d_6-DMSO solution) were not observed in CH$_2$Cl$_2$. The intramolecular hydrogen bonded proton was difficult to detect due to the very low solubility of these compounds combined with the presence of a trace amount of moisture in the solvent (or in the compound) resulting in rapid proton exchange.

Ultraviolet and Visible Spectra

The electronic spectra of all complexes exhibited a strong broad maximum in the region 36,700 to 39,000 cm^{-1}. Similar bands, assigned to a $\pi \rightarrow \pi^*$ transitions in the deprotonated species, with maxima around 37,000 cm^{-1} were observed[28] in H$_2$dmg complexes. The spectra of the complexes reported here resemble those of the corresponding anion with maxima centred at 37,040 cm^{-1} for the H$_2$afdo complexes and at 38,500 cm^{-1} for H$_2$phdo complexes. The extinction coefficients for the 37,040 cm^{-1} band are higher for the macrocycles than the corresponding uncyclized species. The low energy maxima at 22,730 cm^{-1} in H$_2$afdo complexes and around 24,500 cm^{-1} in H$_2$phdo complexes are due to conjugation of the aromatic groups (furyl or phenyl) with the oxime groups of the molecules. Although some of the complexes reported here may have metal-metal interactions in the solid state, the bands arising from such interactions are not expected to be observed in dilute solution. An X-ray structure determination[39] of [Ni(BF$_2$afdo)$_2$ has confirmed BF$_2$ encapsulation with the BF$_2$ groups displaced out of the molecular plane prohibiting close contacts and columnar stacking of the monomeric units.

ACKNOWLEDGEMENTS

One of the authors (M.S.H.) is thankful to the UPM Research Committee for its support of this project.

1. A. Chakravorty, *Coord. Chem. Rev.*, **13,** 1 (1974)
2. R.K. Murman and E.O. Schlemper, *Acta Cryst.* **23,** 667 (1967).
3. M. Galleri, G. Ferraris and D. Vetrbo, *Inorg. Chim. Acta*, **1,** 297 (1967).
4. G. Ferraris and D. Vetrbo, *Acta Cryst.*, **B25,** 2066 (1969).
5. P.G. Lenhert, *Chem. Comm.*, 980 (1967).
6. F.A. Cotton and J.G. Norman, *J. Am. Chem. Soc.*, **93,** 80 (1971).
7. D.E. Williams, G. Wohlauer and R.E. Rundle, *J. Am. Chem. Soc.*, **81,** 775 (1959).
8. M.S. Hussain, B.E.V. Salinas and E.O. Schlemper, *Acta Cryst.*, **B35,** 628 (1979).
9. M.S. Hussain, S.A. Al-Hamoud, M.Z. El-Faer and A. Khan, *J. Coord. Chem.*, **14,** 91 (1985).
10. E. Frasson, C. Panattoni and R. Zammetti, *Acta Cryst.*, **12,** 1027 (1959).
11. E. Frasson, R. Bardi and S. Bezzi, *Acta Cryst.*, **12,** 201 (1959).
12. E. Frasson and C. Panattoni, *Acta Cryst.*, **13,** 893 (1960).
13. K.S. Viswanathan and N.R. Kundur, *Acta Cryst.*, **14,** 675 (1961).
14. C.B. Singh and B. Sahoo, *J. Inorg. Nucl. Chem.*, **36,** 1259 (1974).
15. L. Sugden, *J. Chem. Soc.*, 246 (1932).
16. R. Rereday, *Proc. Phys. Soc (London).*, **44,** 274 (1932).
17. J.B. Willis and D.P. Mellor, *J. Am. Chem. Soc.*, **69,** 1237 (1947).
18. C.V. Bank, R.W.V. Harr and R.P. Vanerwal, *J. Am. Chem. Soc.*, **77,** 324 (1955).
19. T. Matsumoto, T. Koto and K. Shinra, *Nippon Kagaku Zasski*, **86,** 1266 (1955).
20. T.W. Thomas and A.E. Underhill, *Chem. Soc. Rev.*, 99 (1972).
21. R.E. Rundle and M. Parasol, *J. Chem. Phys.*, **20,** 1487 (1952).
22. G.N. Schrauzer, *Ber.*, **95,** 1438 (1962).
23. R.S. Vagg and E.C. Watton, *Acta Cryst.*, **B34,** 2715 (1978).
24. U. Kohler, H.D. Hausen and J. Weidlein, *J. Organometal. Chem.*, **272,** 337 (1984).
25. M. Satake, *Anal. Chim. Acta*, **92,** 423 (1977).
26. V.M. Savostina, O.A. Shpigun and T.V. Chebrekova, *Vestn. Mosk. Univ., Ser. 2 Khim.*, **22** 482 (1981).
27. P.S. Patil and V.M. Shinde, *Mikrochim. Acta*, **2,** 331 (1977).
28. K. Burger, I. Ruff and F. Ruff, *J. Inorg. Nucl. Chem.*, **27,** 179 (1965).
29. F.E. Beamish, *Anal. Chem.*, **33,** 1059 (1961).
30. R. Blinc and D. Hadzi, *J. Chem. Soc.*, 4536 (1958).
31. M.S. Hussain, R.K. Murman and E.O. Schlemper, *Inorg. Chem.*, **19,** 1445 (1980).
32. M.S. Hussain and E.O. Schlemper, *Inorg. Chem.*, **18,** 2275 (1979).
33. M.S. Hussain, E.O. Schlemper and W.M. Yelon, *Acta Cryst.*, **B37,** 347 (1981).
34. E.O. Schlemper, M.S. Hussain and R.K. Murmann, *Acta Cryst.*, **B37,** 234 (1981).
35. M.S. Hussain, *Arabian J. Sci. Engineering.*, **8,** 355 (1983).
36. M.S. Hussain and S.A. Al-Hamoud, *Inorg. Chim. Acta.*, **82,** 111 (1984).
37. M.S. Hussain and E.O. Schlemper, *J. Chem. Soc., Dalton. Trans.*, 751 (1982).
38. M.S. Hussain and E.O. Schlemper, *J. Chem. Soc., Dalton. Trans.*, 750 (1980).
39. M.S. Hussain, M.Z. El-Faer, E.O. Schlemper and A. Khan, *Inorg. Chim. Acta*, **128,** 81 (1987).