JSR Publications

Available Online

J. Sci. Res. **3** (3), 599-607 (2011)

JOURNAL OF SCIENTIFIC RESEARCH

www.banglajol.info/index.php/JSR

Synthesis, Spectroscopic and Electrochemical Studies of Mononuclear Fe(II) and Ni(II) Complexes Containing a Macrocyclic Ligand Derived from Pyridine-2,6-dicarboxaldehyde and 1,2-Bis(2-aminoethoxy) Ethane

M. M. Alam[1*], R. Begum[1], S. M. M. Rahman[2], and I. S. M. Saiful[1]

[1]Department of Chemistry, Shahjalal University of Science and Technology, Sylhet-3114, Bangladesh

[2]Department of Chemistry, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh

Received 9 March 2011, accepted in final revised form 20 June 2011

Abstract

The cyclic (2+2) template condensation of 2,6-pyridinedicarboxaldehyde with 1,2-bis(2-aminoethoxy) ethane using $Pb(SCN)_2$ as the metal source gave dinuclear lead(II) complex, $Pb_2L_1(SCN)_4$ (**1**), where L_1 is tetra-Schiff-base macrocycle. The transmetallation treatment of **1** with suitable metal perchlorate yield $[FeL_1](ClO_4)_2$ (**2**) and $[NiL_1](ClO_4)_2$ (**3**). The complexes (**2** & **3**) have been characterized by elemental analyses, IR, UV-visible, and ESI-MS spectroscopy. Based on spectral data, octahedral geometry may be proposed for these complexes. The electrochemical behavior of iron and nickel complexes is reported.

Keywords: Macrocyclic complexes; Spectroscopic studies; 1,2-Bis(2-aminoethoxy) ethane; Charge transfer.

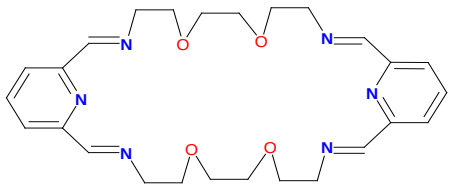
doi: 10.3329/jsr.v3i3.7231 J. Sci. Res. **3** (3), 599-607 (2011)

1. Introduction

Macrocyclic ligands are widely recognized as functional molecules that can bring out the full potential of adapted metal ions. Several excellent examples of universal ligands such as crown ethers [1], porphyrins [2] and saturated (or unsaturated) macrocyclic polyamines [3-5], their chemical properties and functions as metal complexes have been systematically strengthened by the facile and diversified chemical adjustment of their macrocyclic frameworks. Therefore, the design and study of well-arranged metal-containing macrocycles with desirable properties are still a notable achievement. The template condensation reaction lies at the heart of macrocyclic chemistry [6] and has been widely used for synthesis of macrocyclic complexes where, the transition metal ions are

[*] *Corresponding author*: flora2289@yahoo.com, mahbubana-che@sust.edu

used as templating metal agents [7]. Macrocyclic nickel complexes find use in DNA recognition and oxidation [8]. Macrocyclic metal chelating agents are useful for detecting tumor lesions [9]. Prompted by these facts, in the present paper, synthesis and characterization of iron(II) and nickel(II) macrocyclic (L_1) complexes derived from pyridine-2,6-dicarboxaldehyde and 1,2-Bis(2-aminoethoxy) ethane have been discussed. Complexes are characterized using various physio-chemical techniques such as IR, UV-visible, ESI-MS, elemental and electrochemical analyses.



L_1

2. Experimental

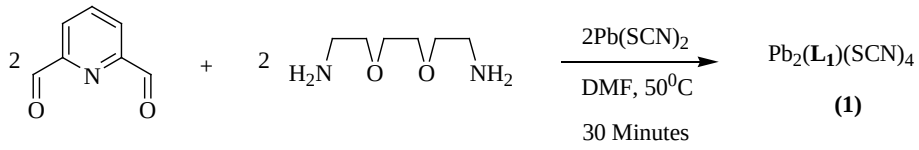
All chemicals are of reagent grade and used without further purification. All measurements were performed at room temperature (25 ± 2 °C). Elemental analyses were carried on JM10 MICROCORDER made by J. Science Laboratory Co., Ltd. IR Spectra were recorded on an Excalibur Series JASCO FT/IR 3000MX/UMA250 Spectrometer in the range of 4000-400 cm^{-1} in KBr pellets. NMR Spectra were measured on Bruker Avance^{III}-400 with $CDCl_3$ as solvent. UV-visible Spectra were recorded on SHIMADZU-1700 UV-Visible Spectrophotometer in CH_3CN solution. The ESI-mass spectrum of complexes was measured with a Quatttro micro API spectrometer made by Waters. Cyclic voltametric measurements were performed using a CV-50W made by BAS.

2.1. *Synthesis of 2,6-pyridine-dicarboxaldehyde*

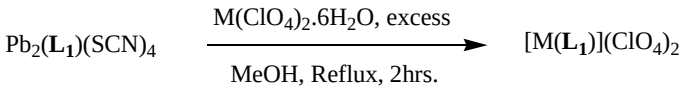
8.122 g (7.3×10^{-2} mol) of SeO_2 was added to 10.186 g (7.3×10^{-2} mol) of 2, 6-bis-(hydroxymethyl) pyridine in distilled dioxane (≈ 200 mL). The reaction mixture was refluxed with stirring at 101° C for 5 hours. The oxide residue was separated from the solution by vacuum filtration on a filtered glass funnel. The light yellow filtrate was concentrated in a rotary evaporator, and then the crude product was dissolved in a minimum amount of chloroform and passed through a short (ca. 12 cm long, ca, 4 cm diameter) silica gel column. About 95 % of crystalline light pink compound was obtained after evaporation of the chloroform. Calc. for $C_7H_5O_2N$: C, 62.22; H, 3.73; N, 10.37 %. Found: C, 61.50; H, 4.39; N, 10.25 %. IR (KBr): ν(C=O) 1716 cm^{-1}, ^{1}H NMR ($CDCl_3$, 400MHz, δ ppm): 10.17 (singlet, 2Ha) 8.18 (doublet, 2Hb), 8.08 (triplet, Hc).

2.2. *Synthesis [12] of $Pb_2L_1(SCN)_4$ (1)*

$Pb(SCN)_2$ (0.438 g, 1.36 x 10^{-3} mol) and 2,6-pyridinedicarboxaldehyde (0.183 g, 1.36 x 10^{-3} mol) were placed in a round bottom flask containing 10 mL of N,N-dimethylformamide (DMF) solution. After complete dissolution of both reagents, a solution (0.201 g, 1.36 x 10^{-3} mol) of 1,2-bis(2-aminoethoxy) ethane was added drop wise. After 30 minutes stirring at 50°C, the yellow reaction mixture was filtered off. Then the diffusion of diethyl ether to the filtrate gave a yellow colored crystalline powder. Yield: 72%, Calc. for $C_{30}H_{34}O_4N_{10}Pb_2S_4$: C, 31.30; H, 3.04; N, 12.17 %. Found: C, 31.34; H, 3.04; N, 12.12 %. IR (KBr): ν(SCN) 2013 cm^{-1} and 2032 cm^{-1}.



Scheme 1. L_1 is Schiff base ligand.



Scheme 2. Preparation of $[M(L_1)](ClO_4)$. Where M = Fe(2) or Ni(3).

2.3. *Synthesis of $[FeL_1](ClO_4)_2$ (2)*

About 25 mL methanol was heated at 60°C for 30 minutes. 0.07g (6.2 x 10^{-5} mol) of compound **1** was then taken in warm methanol and heating was continued for 30 minutes more. 0.023g (6.2 x 10^{-5} mol plus slight excess) of $Fe(ClO_4)_2.6H_2O$ was added to the solution. The reaction mixture was refluxed for 2 hours at 70°C resulting in a deep purple solution. After filtration the solution was concentrated in a rotary evaporator until crystallization started. Recrystallization from acetonitrile and diethyl ether gave a needle like violet crystal. Yield : 30 %. Calc. for $C_{26}H_{34}Cl_2FeN_6O_{12}$: C, 41.67; H, 4.57; N, 11.22 %. Found: C, 41.45; H, 4.58; N, 11.20 %.

2.4. *Synthesis of $[NiL_1](ClO_4)_2$ (3)*

About 50 mL methanol was heated at 60°C for 30 minutes. 0.250 g (2.2 x 10^{-4} mol) of compound **1** was then taken in warm methanol and heating was continued for another 30

minutes. 0.090 g (2.2 x 10^{-4} mol plus slight excess) of $Ni(ClO_4)_2.6H_2O$ was added to the solution. The reaction mixture was refluxed for 2 hours at 70°C resulting in a brown solution**.** After filtration the solution was concentrated in a rotary evaporator until crystallization started. Recrystallization from acetonitrile and diethyl ether gave a needlelike light yellow crystal. Yield = 34 %. Calc. for $C_{26}H_{34}Cl_2NiN_6O_{12}(H_2O)$: C, 40.55; H, 4.71; N, 10.91 %. Found: C, 41.58; H, 4.54; N, 11.15 %.

3. Results and Discussions

The compound **1** was prepared by '2+2' cyclic condensation of 2,6-pyridinedicarboxaldehyde and 1,2-bis(2-aminoethoxy) ethane with high yield. The structure [12] is shown in Fig.1. In this paper R = H and the compound **1** is considered as a new one**.** The needle like crystalline complexes of macrocyclic ligand L_1 with Fe^{2+} and Ni^{2+} were prepared in 30-40% by the reaction of compound **1** with an excess of metal perchlorate in methanol solution. Replacement of Pb^{2+} ion from the macrocycle was fast as judged by instantaneous color change of the reaction mixture. Complex **2** was deep purple whereas complex **3** was light brown in color. The analytical data showed the suggested formula for macrocyclic complexes as $[ML_1](ClO_4)_2$, where M = Fe^{2+} (2) and Ni^{2+} (3) and L_1 = Schiff's base type macrocyclic ligand ($C_{26}H_{34}N_6O_4$). Fig. 1 shows the optimized geometries of the AHE (**a)** 3-21G*, (**b)** 6-31G* (c) 6-31G** results. The structural parameters of these levels were found to be very similar.

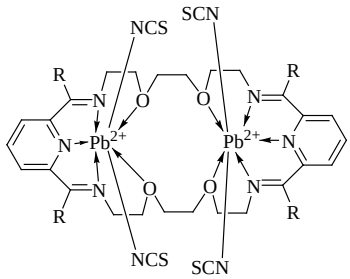


Fig. 1. Structure of $Pb_2L_1(SCN)_4$.

3.1. *ESI-MS spectra*

The formation of $[FeL_1](ClO_4)_2$ (**2)** and $[NiL_1](ClO_4)_2$ (**3)** complexes was confirmed by ESI-MS spectrometry. The positive ion mass spectrum was measured in CH_3CN solution. In both cases the spectra consist of almost 100% of the major peak of $[ML_1]^{2+}$. We also simulated the peak with almost less than 1% compared to major peak intensities which is unstable $[ML_1](ClO_4)^+$ ion. The isotope patterns of the complexes were simulated using i-Mass software and then compared with measured one. Measured and calculated isotope patterns of the complex and complex ions are shown in Figs. 2 to 5.

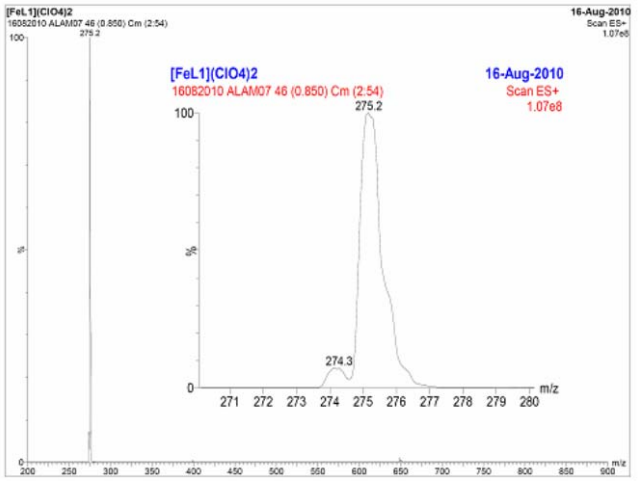


Fig. 2. The original ESI-MS spectra of $[FeL_1](ClO_4)_2$(2) measured in CH_3CN.

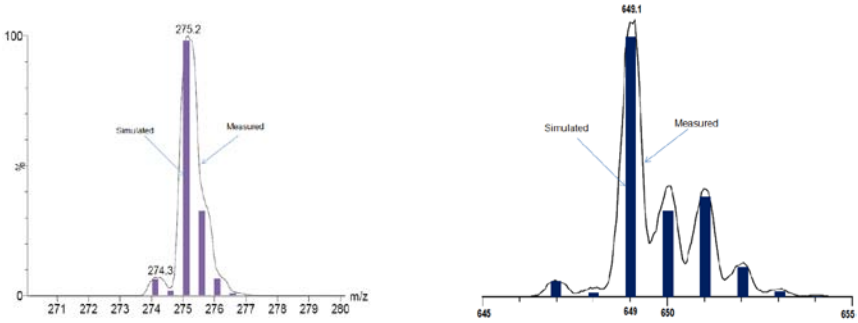


Fig. 3. ESI-MS spectra of (a) $[FeL_1]^{2+}$ and (b) $[FeL_1](ClO_4)^+$ ion measured in CH_3CN.

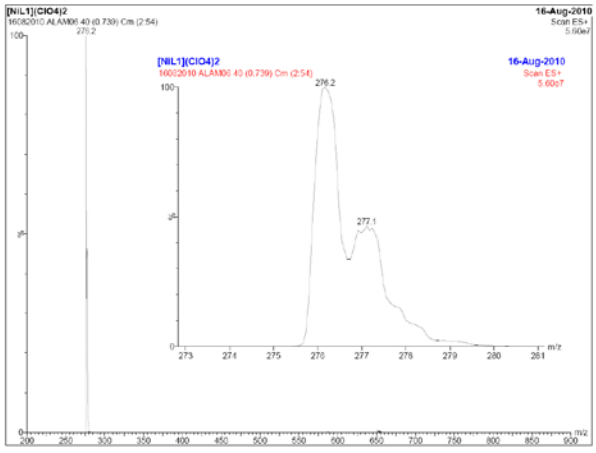


Fig. 4. The original ESI-MS spectra of $[NiL_1](ClO_4)_2$(3) measured in CH_3CN.

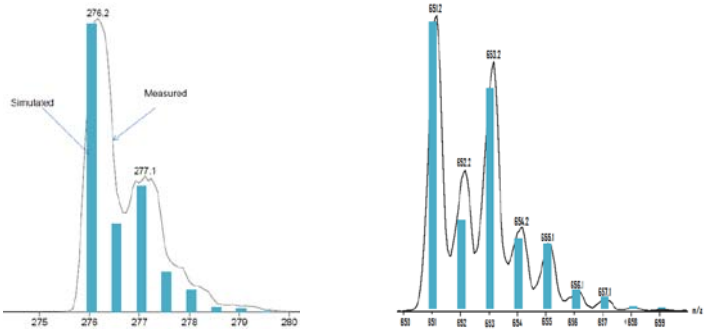


Fig. 5. ESI-MS spectra of (a) $[NiL_1]^{2+}$ and (b) $[NiL_1](ClO_4)^+$ ion measured in CH_3CN.

The ESI-MS spectral data analysis of these complexes are shown in Table 1. The data were in a good agreement with the proposed formula for these complexes, i.e.,$[ML_1](ClO_4)_2$. This suggests the formation of macrocyclic frame as shown in Fig. 6.

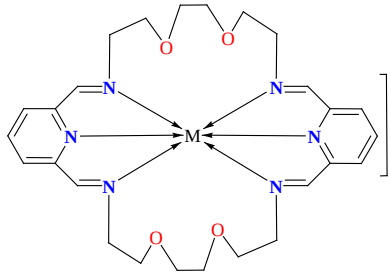


Fig. 6. $[ML_1]$, where, M = Fe(II) and Ni(II).

Table 1. ESI-MS spectral data of the divalent iron and nickel complexes.

Complexes	Molecular weight (g/mol)	Important peaks due to complex fragmentation
$[FeL_1](ClO_4)_2$ (2)	749.33	$[FeL_1](ClO_4)^+ = 649.1$ $[FeL_1]^{2+} = 275.2$
$[NiL_1](ClO_4)_2$ (3)	752.18	$[NiL_1](ClO_4)^+ = 651.2$ $[NiL_1]^{2+} = 276.2$

3.2. *Infrared and electronic spectra*

The important infrared frequencies appeared in the complexes are given in Table 2. The IR spectra of the complexes indicated that the macrocycle has remained unchanged during the metal exchange reaction. In the spectrum although many differences are observed but

there is also similarity with $Pb_2L_1(SCN)_4$. Absence of absorption band at 3200-3400 cm^{-1} indicates that hydrolysis to amine and carbonyl compound had not occurred. In $Pb_2L_1(SCN)_4$ two strong bands appeared at 2013 and 813cm^{-1} is due to SCN^--centered absorption [10]. The strong bands at 1620-1660 and 1580-1600 cm^{-1} are assigned to ν(C=N) and the highest-energy pyridine ring vibration, respectively [11, 12].

Table 2. Characteristic IR frequencies (cm^{-1}) of the complexes.

Complexes	ν(SCN^-)	ν(C-H)	ν(C=N)Py	ν(ClO_4^-)
$Pb_2L_1(SCN)_4$(1)	2013s 813m	2870m	1654s 1585s	---
$[FeL_1](ClO_4)_2$(2)	---	2947m	1616w	1092s 910m 625s
$[NiL_1](ClO_4)_2$(3)	---	2943m 2877m	1589s	1091s 922s 624s

The intensities and position of ν(C=N) and pyridine-modes in Fe^{2+} complex have been changed compared to Ni^{2+} complex. This change is associated with the fact that Fe^{2+} ion is low spin. Such effect has been obsrved in low-spin Fe^{2+} complexes of α-di-imine ligands [5]. The strong bands of ClO_4^- appeared at 1090 and 620-625 cm^{-1}, respectively, are unsplit and characteristic bands of uncoordinated ion [10,13, 14]. In both complexes 2 and 3, the absence of peak at around 650 to 700 cm^{-1} region supported the presence of uncoordinated perchlorate ion. The electronic spectra (Fig. 7a) of Fe^{2+} complex consist of two intense bands at 474 nm and 599 nm characterized the spectra as being charge transfer in origin. This spectrum is very similar to that of Fe^{2+} complex of the tridentate ligand 2-(2`-pyridylmethyleneaminomethyl)pyridine [15]. We therefore assign them to transitions of the metal t_{2g} electrons to the pπ* antibonding orbitals of the ligand. These data thus support the proposed octahedral structure. In case of Ni^{2+} complex no such bands were appeared as shown in Fig. 7b.

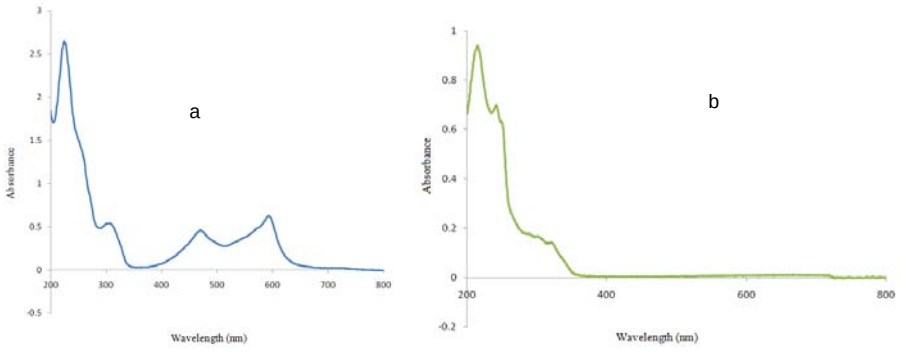


Fig.7. UV-visible spectrum of a) $[FeL_1](ClO_4)_2$ (2) and b) $[NiL_1](ClO_4)_2$ (3).

3.3. *Electrochemical measurement*

The electrochemical properties of $[FeL_1](ClO_4)_2$ (2) and $[NiL_1](ClO_4)_2$ (2) evaluated by cyclic voltametry measurements in CH_3CN are shown in Fig. 8 . Two redox waves were observed for Fe^{2+} complex in the range of +2.0V to -2.1V. The most positive wave is ascribed to a redox process occurring at the metal, Fe^{3+} to Fe^{2+}. The other redox process occuring between -1.4V to -1.85V is assigned to form Fe^{2+}-ligand interaction. The assignment is the electron moved from metal to ligand pπ* orbitals and delocalized onto the trimethine units which point out to involve trimethine part as a coordinating group [16]. For Ni^{2+} complex, the redox wave was observed at +1.37 V in the potential window of CH_3CN describing the Ni^{3+}/ Ni^{2+} couple.

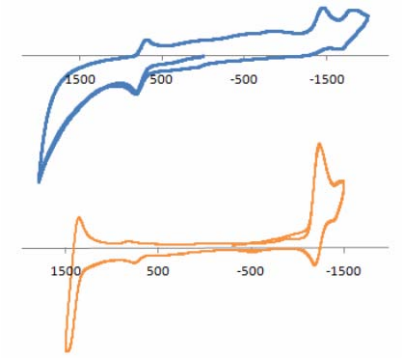


Fig. 8. Cyclic voltammogram of $[Fe(L^1)](ClO_4)_2$ complex (upper) and of $[Ni(L^1)](ClO_4)_2$ (below) in CH_3CN at 25^0C. E/V vs Ag/Ag+. 1 mM / 0.10 M (Sample/TBAP). Scan rate 0.050 V/S.

4. Conclusion

The macrocyclic ligand L_1 exhibited mononucleating properties with metal ions Fe^{2+} and Ni^{2+}. Analytical data, spectroscopic analysis, cyclic voltametry, and ESI-MS suggested that the complexes **2** and **3** have octahedral geometry with only the pyridine and azo-methine nitrogen atoms of the macrocycle are coordinated with the metal ions. The six coordination property of iron(II) and nickel(II) were favored due to the large crystal field stabilization energy. The perchlorate ion acted as counter ions in complexes **2** and **3**. The complexing behavior was in contrast with that of Pb^{2+} ion (complex **1**). The macrocycle showed binucleating behavior towards lead(II) and different coordination properties. In complex **1** each Pb^{2+} ion showed coordination with three nitrogen (one from pyridine and two from azo-methane), two oxygen from the macrocycle, and two nitrogen from SCN^-.

Acknowledgements

We thank Professor Dr. Eiji Asato, Department of Chemistry, University of the Ryukyus, Okinawa, Japan for his kind permission to conduct all the measurements. We are grateful

to Mr. Gima Shin-Ichi and Mr. Yuto Teruya for their direct help to measure UV, CV, IR and ESI-MS. Thanks are also to Dr. Md. Anwar Hossain Khan and Dr. Satoshi Takara for their mental and technical support.

References

1. G. W. Gokel, W. M. Leevy, and M. E. Weber, Chem. Rev. **104**, 2723 (2004). doi:10.1021/cr020080k
2. P. Hambright, Coord. Chem. Rev. **6**, 247 (1971). doi:10.1016/S0010-8545(00)80041-7
3. E. Kimura, Tetrahedron **48**, 6175 (1992). doi:10.1016/S0040-4020(01)88212-0
4. D. H. Busch, Acc. Chem. Res. **11**, 392 (1978). doi:10.1021/ar50130a005
5. H. H. Zhang, J. S. Bradshaw, and R. M. Izatt, Chem. Rev. **97**, 3313 (1997). doi:10.1021/cr960144p
6. N. F. Curtis, Coord. Chem. Rev. **3**, 3 (1968). doi:10.1016/S0010-8545(00)80104-6
7. M. S. Niasari and F. Davar, Inorg. Chem. Commun. **9**, 175 (2006). doi:10.1016/j.inoche.2005.10.028
8. J. G. Muller, X. Chen, A. C. Dadiz, S. E. Rokita, and C. J. Burrows, Pure Appl. Chem. **65**, 545 (1993). doi:10.1351/pac199365030545
9. C. Kosmos, D. Snook, C. S. Gooden, L. N. S. Courtenay, M. J. McCalla, C. F. Meares, and A. A. Epenetos, Cancer Research **52**, 904 (1992).
10. K. Nakamoto, Infrared And Raman Spectra of Inorganic and Coordination Compounds, Part B, Applications in coordination, organometallic, and bioinorganic chemistry, 6th ed. (Wiley, Nov 2008) p. 88.
11. M. G. B. Drew, A. H. Bin Othman, S. G. McFall, P. D. A. McIlory, and S. M. Nelson, J. C. S. Dalton Trans. 1173 (1977).
12. M. G. B. Drew, A. Rodgers, M. McCann, and S. M. Nelson, J. Chem. Soc., Chem. Comm. 415 (1979).
13. H. Z. Siebert, Anorg. Allg. Chem. **275**, 225 (1954). doi:10.1002/zaac.19542750407
14. D. L. Lewis, E. D. Estes, and D. J. Hodgson, J. Cryst. Mol. Struct. **5**, 67 (1975). doi:10.1007/BF01202553
15. P. Krumholz, Inorg. Chem. **4**, 757 (1965). doi:10.1021/ic50027a036
16. S. M. Nelson, Pure & Appl. Chem. **52**, 2461 (1980). doi:10.1351/pac198052112461