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Synthesis, Characterization and X-ray Crystal Structure of the Dimer Complex[Cu (PLITSC-2H) $(NH_3)]_2 \cdot 2H_2O$

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Abstract The title complex$[Cu(ITSCPL\text{-}2H)(NH_3)]_2 \cdot 2H_2O$ (1), is reported. The structure of the title compound, C20 H34 Cu2 O6 N10 S2 as an interesting metal complex with a Schiff base derived from isothiosemicarbazide and pyridoxal (3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carboxaldehyde) is reported. Ligand pyridoxal-S-methyliso thiosemicarbazone (PLITSC; H_2L) is tridentate ONN ligand. The Cu^{II} environment is a square planar coordination, the equatorial plane of which is formed by the tridentate ONN-coordinated pyridoxal-Smethyliso thiosemicarbazone and one amonium molecule. This compound crystallizes in triclinic symmetry, in space group P-1, with lattice constans: a = 9.0161(2)Å, b = 10.9078(3)Å, c = 16.6355(5)Å, α = 105.1276(12)°, β = 90.9785(10)°, γ = 111.0567(13)°, V = 1462.68(7) $Å^3$, Z = 3, F(000) = 742, R1 = 0.0452, wR2 = 0.1110. The crystal structure, molecules are linked by O-H…O, N-H…O and C-H…O contacts. The complex was characterized by elemental analysis, IR spectra, conductometric and magnetochemical measurements, and X-ray diffraction.

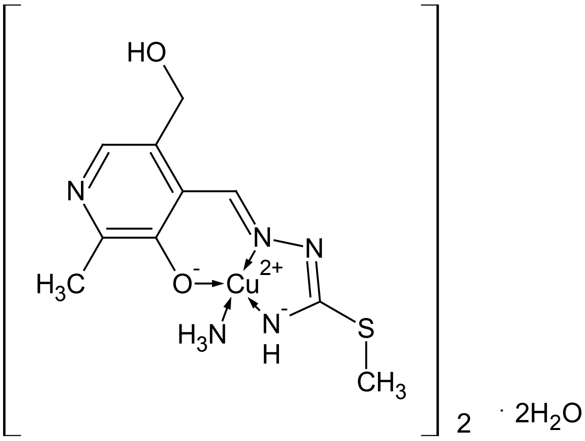
Keywords Pyridoxal-S-methyliso thiosemicarbazone, Ni(II) complex, Synthesis, Characterisation, Crystal structure

1. Introduction

Transition metal complexes with ligand based on thiosemicarbazides (TSC) have been studied for many years because of their interesting structural properties and biological activities[1,2]. The complexes with TSC-based ligands exhibit a wide range of biologically important properties, such as antiviral, antitumor and anti-inflammato ryactivities[3,4]. Isothiosemicarbazones (ITSC) can also act as biologically active antibacterial agents[5].

There are many complexes incorporating the pyridoxal-S-methyliso thiosemicarbazone (PLITSC) ligand in its tridentate ONN coordination mode and the most important results gained in studying these types of complexes have been reviewed by Leovac[6]. Almost all of the reported complexes including several Fe-base compounds such as $[Fe(ITSCPL)(ITSCPL\text{-}H)](NO_3)_3$, $[Fe(ITSCPL)Cl_3] \cdot H_2O$ and$[Fe(ITSCPL)_2]OAc \cdot 2H_2O$[7,8] were characterized by physical properties (elemental (C,H,N) analysis, molar conductivities) and their voltametric properties. It is worth noting that the syntheses and characterizations of several of these complexes were also included as a topic of a PhD thesis[9].

However, the only X-ray characterized complex that incorporates PLITSCligand is $[Cu^{II}(NO_3)(PLITSC)(H_2O)](NO_3)^a$ and$[Ni(PLITSC)(H_2O)_3](NO_3)_2^b$[10]. The PLITSC ligand acts as a tridentate ligand in this Cu^{II} complex forming two fused chelate rings, one being five-membered (ITSC) and one six-membered (PL). The PLITSC ligand in the title complex **1** is coordinated in the same manner as the reported for the Cu^{II} complex.



Scheme 1. Complex 1

It is worth nothing that the PLITSC ligand can adopt three different forms when coordinated to a transition metal namely neutral H_2L, monoanionic HL^- or dianionic L^{2-} forms (see Scheme 2).

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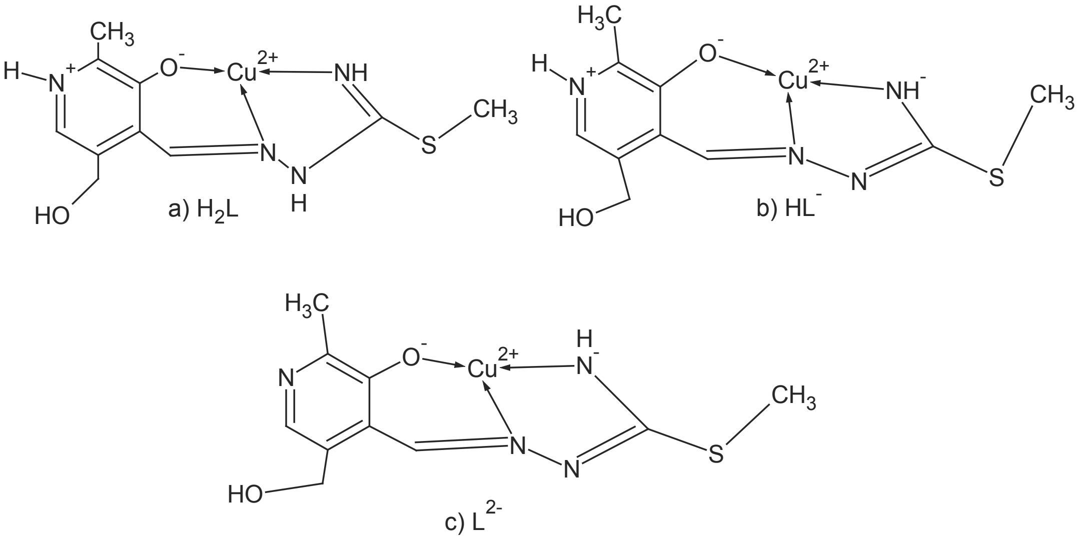


Scheme 2. Coordination models and ligand forms: a) neutral, b) mono- and c) dianionic

The neutral form H_2L is zwitterionic formed by the proton migration from the phenolic OH group to the heterocyclic nitrogen atom. The monoanionic form HL^- is formed by deprotonation of the hydrazine nitrogen atom of the isothiosemicarbazide residue. Further deprotonation of the pyridine nitrogen atom leads to the formation of the actually dianionic form L^{2-}. Moreover, the PLITSC ligand usually acts as a tridentate ligand by coordinating to metal centers via phenolic oxygen, hydrazine and amido nitrogen atoms. Furthermore, the isothiosemicarbazide (ITSC) moiety exists in the imido form as shown in several other examples[11].

2. Experimental Section

2.1. Physical Measurements

All commercially obtained reagent-grade chemicals were used without further purification, except for the ligands, which were prepared according to the previously described procedures[8]. Elemental (C,H,N) analysis of air-dried samples was carried out by standard micromethods in the Center for Instrumental Analysis, Faculty of Chemistry, Belgrade. Magnetic susceptibilities were measured at room temperature using a magnetic susceptibility balance MSB-MKL (Sherwood Scientific Ltd. Cambridge, England). Molar conductivities of the freshly prepared 1×10^{-3} M solution were measured on a Jenway 4010 conductivity meter. IR spectra (KBr disk) were recorded on a Thermo Nicolet (NEXUS 670 FT-IR) instrument. The X-ray analysis was performed in Oxford Chemical Crystallography Service.

2.2. Preparation of the Title Compound

The pyridoxal 3-methylisothiosemicarbazone ligand, H_2L, was prepared by the reaction of an ethanolic solution of 3-methylisithiosemicar-bazidehydroiodide with pyridoxal hydrochloride, and subsequent neutralisation with an aqueous solution of Na_2CO_3. Brown single crystals of **1** were obtained by the reaction of a hot methanol solution of the ligand with $CuSO_4{\cdot}5H_2O$ (molar ratio 1:1). NH_3 should be intercalated into stirred solution in the drops until it becomes transparent. Yield: 74%. μ_{eff}= 1.32 BM; elemental analysis calcd. (%) for $C_{20}H_{34}Cu_2N_{10}O_6S_2$: C 33.37, H 5.04, N 19.46; S 8.91; found: C 33.38, H 5.09, N19.96; S 8.53. $\lambda_{M(DMF)}$= 1.6 Scm 2 mol^{-1}. IR (KBr, Nujol) Suporting material.

2.3. X-ray Crystallography

A single crystal of 0.01 x 0.01 x 0.01 was mounted on a glass fiber in a random orientation. Data collection was performed at temperature 150 K on a computing data collection Nonius Kappa CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073Å). Data collection and cell refinement were carried out 106 using SIR92[12] and DENZO and COLLECT[13]. The structure of 107 compound 1 was solved with SIR-92 and refined using 108 CRYSTALS[14, 15]. In general, the hydrogen atoms were 109 visible in the difference map. Hydrogen atoms bound to carbon were initially positioned geometrically while the hydrogen atoms for the coordinated water molecules were located in the difference map. All hydrogen positions and isotropic displacement parameters were then refined in a separate cycle, using restraints prior to inclusion into the model with riding constraints. Hydrogen positions were checked for feasibility by examination of the hydrogen-bonding network. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge by writing to the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK;e-mail:depos-it@ccdc.cam.ac.uk. The CCDC deposition number is 754806.

Crystal data and details concerning data collection and structure refinement are given in Table 1.

Table 1. Crystal data and structure refinement for complex (1)

Identification code	global
Empirical formula	C13.33 H23.33 Cu1.33 N6.67 O4.67 S1.33
Formula weight	479.19
Temperature	150 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 9.0161(2) Å a= 105.1276(12)°. b = 10.9078(3) Å b= 90.9785(10)°. c = 16.6355(5) Å g = 111.0567(13)°.
Volume	1462.68(7) Å^3
Z	3
Density (calculated)	1.632 Mg/m^3
Absorption coefficient	1.654 mm^{-1}
Max. and min. transmission	0.85 and 0.72
Refinement method	Full-matrix least-squares on F^2
Data / restraints/parameters	6645 / 0 / 370
Goodness-of-fit on F^2	0.9119
Final R indices[I>2sigma (I)]	R1 = 0.0452, wR2 = 0.1110
R indices (all data)	R1 = 0.0658, wR2 = 0.1229
Largest diff. peak and hole	0.89 and -0.87 e.Å^{-3}

3. Results and Discussion

Regarding the majority of Cu(II) complexes (which are coloured green), complex is distinguishable by its characteristically dark colour. Cu(II) complexes have similar characteristics (colour) with tridentate ONN salicylaldehyde S-*methylisothiosemicarbazone* (H_2L) as well, which are green, with the exception of $Cu(L)NH_3{\cdot}H_2O$ which is dark-coloured[16]. Complex 1 has reduced μ_{eff} (1.32) value, which can be explained by its dimeric structure, most often realized via oxygen atoms of phenolic hydroxyl. These oxygen atoms function as bridges[17] in case of tridentate ONN isothiosemicarbazones.

The examined complex is badly dissoluble. It can be dissolved in DMF, while $\lambda_{M(DMF)}$ = 1.6 value indicates its *non-electrolytic nature*[18].

IR spectrum of$[Cu(ITSCPL-2H)(NH_3)]_2{\cdot}2H_2O$ complex has no prominent bands[19] at about 2800cm^{-1}, which can be understood, as regards deprotonation of pyridine nitrogen atom.

X-ray analysis of$[Cu(ITSCPL-2H)(NH_3)]_2{\cdot}2H_2O$ (1), showed a square planar structure, formed by the tridentate ONN coordination of the PLITSC ligand and one NH_3 molecules.

The title compound crystallizes in the space group P-1. The molecular structure and atom-numbering scheme are show in Fig.1.

The analysis of the crystal structure of **1** has been carried out and experimental details are presented, whereas its geometrical features (bond distances and angles) are given in Table 2 and in Table 3 are given possible hydrogen bonds.

Table 2. Bond lengths[Å] and angles[°] for complex (1)

Cu(1)-O(2)	1.886(2)	O(2)-Cu(1)-N(6)	93.03(10)
Cu(1)-N(6)	1.948(3)	O(2)-Cu(1)-N(9)	173.28(11)
Cu(1)-N(9)	1.934(3)	N(6)-Cu(1)-N(9)	80.92(12)
Cu(1)-N(19)	2.003(3)	O(2)-Cu(1)-N(19)	89.47(11)
O(2)-C(3)	1.307(4)	N(6)-Cu(1)-N(19)	177.41(12)
C(3)-C(4)	1.417(4)	N(9)-Cu(1)-N(19)	96.62(13)
C(3)-C(15)	1.425(5)	Cu(1)-O(2)-C(3)	127.4(2)
C(4)-C(5)	1.444(5)	O(2)-C(3)-C(4)	125.2(3)
C(4)-C(12)	1.424(5)	O(2)-C(3)-C(15)	117.0(3)
C(5)-N(6)	1.289(4)	C(4)-C(3)-C(15)	117.7(3)
C(5)-H(51)	0.934C	C(3)-C(4)-C(5)	123.0(3)
N(6)-N(7)	1.401(4)	C(3)-C(4)-C(12)	118.0(3)
N(7)-C(8)	1.331(4)	C(5)-C(4)-C(12)	118.9(3)
C(8)-N(9)	1.317(4)	C(4)-C(5)-N(6)	123.4(3)
C(8)-S(10)	1.768(3)	C(5)-N(6)-Cu(1)	127.3(2)
S(10)-C(11)	1.804(4)	C(5)-N(6)-N(7)	117.3(3)
Cu(20)-O(21)	1.885(2)	Cu(1)-N(6)-N(7)	115.4(2)
Cu(20)-N(25)	1.956(3)	N(6)-N(7)-C(8	108.4(3)
Cu(20)-N(28)	1.938(3)	N(7)-C(8)-N(9)	123.7(3)
Cu(20)-N(38)	1.985(3)	N(7)-C(8)-S(10)	112.0(2)
O(21)-C(22)	1.302(4)	N(9)-C(8)-S(10)	124.3(3)

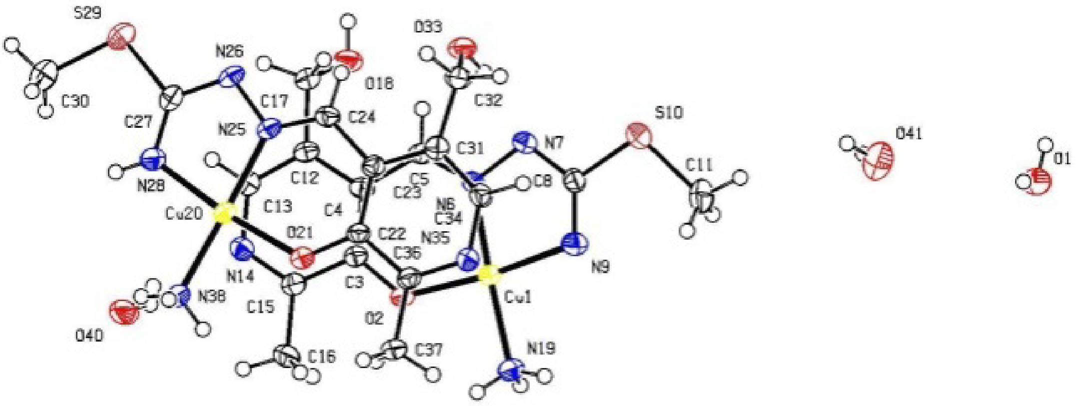


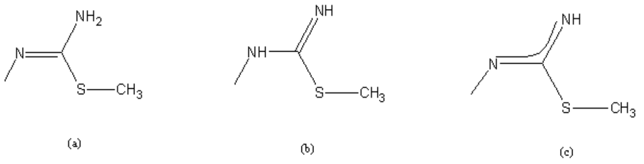
Figure 1. Complex 1

Table 3. Hydrogen bonds for complex (1)[Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)<(DHA)
O(18)-H(181)...O(40)#2	0.82	1.88	2.676(5) 163
N(38)-H(383)...O(33)#3	0.89	2.13	2.979(5) 158
N(19)-H(193)...N(7)#4	0.88	2.35	3.110(5) 145
N(19)-H(192)...O(41)#5	0.87	2.20	3.037(5) 161
C(30)-H(301)...O(1)#6	0.96	2.56	3.503(5) 169
C(11)-H(112)...C(3)#4	0.96	2.56	3.515(5) 171
O(33)-H(331)...N(7)	0.80	2.04	2.829(5) 170
N(38)-H(382)...O(1)#4	0.88	2.11	2.977(5) 167
O(41)-H(411)...O(18)#	0.82	2.02	2.836(5) 172
O(40)-H(401)...N(14)	0.84	2.00	2.800(5) 160
O(1)-H(11).......N(26)#8	0.81	2.19	2.994(5) 174
O(1)-H(22)......O(40)#4	0.80	2.18	2.963(5) 165
N(38)-H(381)...N(26)#1	0.90	2.32	3.121(5) 149

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+3,-z+2 #2 x+1,y,z #3 x-1,y,z #4 -x+1,-y+2,-z+1
#5 -x+1,-y+1,-z+1 #6 x,y+2,z+1 #7 x,y-1,z
#8 -x+2,-y+2,-z+1

Ligand is present in L^{2-}form in complex 1, so that square-planar environment around Cu constitutes tridentate ONN ligand and the nitrogen atom in an ammonia molecule. The shortest Cu-ligand bond (Cu1(20)-O2(21) (1.886Å, 1.885Å)) is present between copper and oxygen atom of deprotonated phenolic hydroxyl. Bonds between Cu atoms and ammonium nitrogen atoms of Cu1(20)-N19(38) (2.003Å, 1.985Å) are very similar to bibliographic sources[20]. With reference to the bonds within ligands, it is interesting to compare the bonds in the isothiosemicarbazone fragment. Data belonging to X-ray analyses of a large number of metal complexes with isothiosemicarbazones and thiosemicarbazones show that the uncoordinated neutral ligands are present in the amido form, while coordinated neutral ligands can be found in the imido form[17] (see Scheme 3).



(a) (b) (c)

Scheme 3. Amido (a), imido- (b) and deprotonated (c) forma of ITSC

This fragment is deprotonated in complex. As in $[Cu^{II}(NO_3)(PLITSC)(H_2O)](NO_3)^a$ and $[Ni(PLITSC)(H_2O)_3](NO_3)_2^b$[10] complexes, the distance between carbon atoms and terminal nitrogen atoms is obviously shorter (1.278(3) Å; 1.287(4) Å) than distance of carbon atom with theadjacent hydrazine nitrogen atom (1.366(3) Å1.370(4) Å), in which process the first bond is similar to twofold C=N bond. In the case of complex, deprotonation of hydrazine nitrogen atom results in delocalization of the electron density (Scheme 3) and thereby lessening differences in the bond lengths between C atoms and adjacent N atoms, N7(26)-C8(27) (1.331Å,1.345Å), C8(27)-N9(28) (1.316Å, 1.326Å). Deprotonation of pyridine nitrogen N14(35) has no influence on the distances between adjacent C-N bonds, but consequently influences the angle formed by adjacent C atoms, diminishing it from the value of 124° (protonated form) to the value of 118.67° (118.69°), which is the current amount.

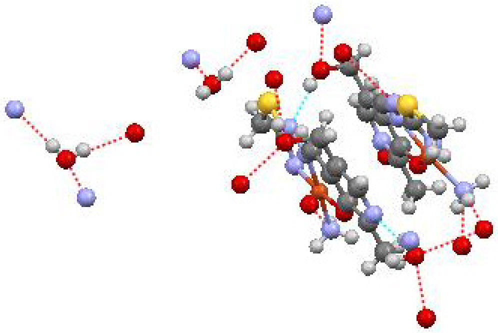


Figure 2. Packing arrangement between two asymmetric units and several intermolecular hydrogen bonding interactions

4. Conclusions

The synthesis, characterisation and structural analysis of Cu complexes incorporating PLITSC ligand is described. The Cu^{II} environment is a square planar coordination, the equatorial plane of which is formed by the tridentate ONN-coordinated PLITSC ligand and one ammonium molecule. This compound crystallizes in triclinic symmetry, in space group P-1.

5. Supplementary Information

Crystallographic data (excluding structure factors) for the structure (**1**) reported in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 754806. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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REFERENCES

[1] West, D. X. , Padhye, S. B., and Sonawane, P. B., Structure and Bonding, Berlin, Springer-Verlag, Vol. 76 pp.1-4, 1999.

[2] Casas, J. S, Garcia-Tasende, M. S., and Sordo, J., 2000, Coordination Chemistry Review209, 197.

[3] West, D. X., Liberta, A. E., Padhye, S. B., Chikate, R. C., Sonawane, P. B., Kumb-har, and A.S., Yeranade, R. G., 1993, CoordinationChemistry Review123,49.

[4] Belicchi Ferrari, M., Bisceglie, F., Casoli, C., Durot, S., Morgenstern-Badarau, I., Pelosi, G., Pilotti, E. , Tarasconi, P., 2005, Journal Medicinal Chemistry 48, 1671.

[5] Cardia, M.C., Begal, a M., Delogu, A., Maccioni, E., and Plumitallo, A., 2000, Farmaco 55,93.

[6] Leovac, V., Jevtovic, V., Jovanovic, Lj., and Bogdanovic, G., 2005, Journal Serbian Chemical Society, 70, 393.

[7] Jevtovic, V., Jovanovic, Lj., Leovac, V., and Bjelica, L., 2003, Journal Serbian Chemical Society ,68,929.

[8] Jovanovic, Lj., Jevtovic, V., Leovac, and V., Bjelica, L., 2003, Journal Serbian Chemical Society,70,187.

[9] Jevtovic, V. S., 2002, Ph.D. Thesis, Faculty of Science, University of Novi Sad, 90 p.

[10] [a]Leovac, V., Jevtovic, V., Bogdanovic, G.. 2002, Acta Crystallographica C58, m514. [b]Jevtovic, V., and Vidovic, D., 2010, Journal of Chemical Crystallography, 40, 9, 794-798.

[11] Novakovic, S., Tomic, Z., Jevtovic, and V., Leovac, V., 2002, Acta Crystallographi-ca, C58, m358.

[12] Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M.C., Polidori G, and Camalli, M., SIR 92- a program for automatic solution of crystal structures by direct methods, 1994, Journal Applied Crystallography, 27, 435.

[13] Otwinowski, Z., & Minor, W., in Methods Enzymology, edited by Carter, C. W. and Sweet, R. M., 1996, Academic Press, New York, USA.

[14] Nonius, Delft, B. V., 1997, The Netherlands.

[15] Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, J., and Watkin, D. J., CRYSTAL version 12: software for guided crystal structure analysis, 2003, Journal Applied Crystallography, 36,1487.

[16] Leovac, V., Ph.D. Thesis, Faculty of Science, University of Novi Sad, 121 p.

[17] Leovac, V., and Cesljevic, V., Koordinaciona hemija izotiosemikarbazida i njegovih derivata, Univerzitet Novi Sad, 2002.

[18] Geary,W. J., 1971., Coordination Chemistry Review, 81-122.

[19] Ferrari, M. B., Fava, g. G., Leporati, E., Pelizzi, G., Tarasconi, P., and Tosi, G., 1986, Journal Chemical Society Dalton Transition, 2455.

[20] Hathaway, B.J., 1987, Cooper incomprehensive Coordination Chemistry, (Eds. G. Wilkinson, R. D. Gillard, J. McClevery) Pergamon Press, Oxford, 3, 53.