DALTON

Co-ordination of copper(II) and nickel(II) ions by a novel open chain oxime ligand

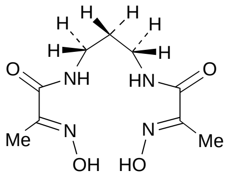
Anna M. Duda,[a] Aldona Karaczyn,[a] Henryk Kozłowski,*,[a] Igor O. Fritsky,[b] Tadeusz Głowiak,[a] Elena V. Prisyazhnaya,[b] Tatiana Yu. Sliva[b] and Jolanta Świątek-Kozłowska[c]

[a] *Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50383 Wrocław, Poland*
[b] *Department of Chemistry, Shevchenko University, Kiev 252033, Ukraine*
[c] *Department of Basic Medical Sciences, School of Medicine, 51601 Wrocław, Poland*

Potentiometric spectroscopic and X-ray studies of the open chain oxime ligand, *N*,*N′*-bis(2-hydroxyiminopropionyl)propane-1,3-diamine and its complexes with Ni^{II} and Cu^{II} ions showed a very high efficacy of the ligand studied in the co-ordination of both Cu^{II} and Ni^{II} ions. The metal complexes are very stable and square-planar with four nitrogens involved in metal-ion binding. These complexes may be additionally stabilised by hydrogen bonds between two oxime oxygen atoms.

There is growing interest in the molecular design and co-ordination chemistry of structurally modified bioligands containing several different donor groups. One example of this approach is substitution of the amino group in amino acids or peptides by a hydroxyimino group. Recently we reported results on the study of oxime analogues of amino acids and dipeptides where such an approach has been applied.[1,2] Presently the increasing interest in the investigation of co-ordination properties of polyfunctional ligands containing hydroxyimino groups has grown from several different perspectives. Traditionally, oximes have been extensively used in analytical chemistry and metallurgy as very effective complexing agents for the purposes of isolation, separation and extraction of different metal ions. Molecular design of multidonor ligands containing other strong donor groups along with the oxime function may lead to new, very effective, chelating agents. One fascinating example of this approach is the modification of the poorly co-ordinating carboxylic group into a hydroxamic moiety which leads to one of the most powerful donors found in biological systems.[3] Secondly, the co-ordinated oxime groups appear to be suitable matrices in which to conduct versatile organometallic reactions, resulting in different heterocyclic compounds, thus much effort has been made in recent years studying the reactivity of the co-ordinated oxime groups.[4] The capacity of the oximato group to co-ordinate additional metal ions *via* the bridging N and O functions and the fact that the oxime bridges were established to mediate exchange interactions between paramagnetic centers very effectively provoked the start of a wide usage of oxime ligands in molecular magnetism for the design and synthesis of polynuclear assemblies.[5] Finally, the interest in oxime-containing co-ordination compounds is constantly increasing in connection with the biological implication of oximes (especially, as intermediates in the biosynthesis of nitrogen oxide[6]) and the marked and versatile bioactivity indicated by different oximes and their metal complexes. It is important to note that the realization of the biological function of oximes and the mechanism of their metabolism in living systems are evidently connected with their chelation by metal ions. For example, oximes were found to act as strong inhibitors of *arginase*.[7] This effect is connected with co-ordination of the N=OH group of the inhibitors to the *arginase* Mn^{2+}-containing active center.

The binding mode of the oxime group depends to a great extent not only on the nature of the metal ion but on the presence of a neighbouring donor group in the same ligand. The combination of these two moieties results in stable chelate rings upon co-ordination to a metal ion. In the case of oxime complexes with late 3d and platinum-group metals one of the most effective groups whose presence leads to a very strong complexation with metal ions is the amide group adjacent to an oxime moiety. Earlier we reported the results of solution and solid-state studies of copper(II) and nickel(II) complexes with 2-(hydroxyimino)propanamide, $CH_3C(=NOH)C(O)NH_2$,[1,2] and 2-cyano-2-(hydroxyimino)acetamide, $NCC(=NOH)C(O)NH_2$.[8] In a continuation of this research we have expanded our efforts on the design and synthesis of a series of open chain ligands involving two amide and oxime moieties each in one molecule.



We report here the synthesis, structure and characterization of copper(II) and nickel(II) complexes with a novel open chain oxime ligand *N*,*N′*-bis(2-hydroxyiminopropionyl)propane-1,3-diamine (H_2pap) along with potentiometric and spectroscopic studies of complex formation in aqueous solution. The properties of this ligand are expected to differ from those of 2-(hydroxyimino)propanamide (Hpox) and its derivatives studied before mostly because of steric reasons. The presence of a trimethylene bridge between two Hpox moieties results in the ligand H_2pap with a tetradentate co-ordination mode and thus stronger chelation to metal ions.

Experimental

Syntheses

All chemicals were commercial products of reagent grade and used without further purification. Elemental analyses (C, H and N) were conducted by the Microanalytical Service of the University of Wrocław. Copper and nickel contents were determined by atomic absorption spectroscopy.

H_2pap. The ligand was synthesized analogously to the reported method for *N*,*N′*-bis(2-hydroxyiminopropionyl-propane)-1,2-diamine.[9] Ethyl pyruvate (13.1 g, 0.1 mol) was dissolved in methanol (50 ml), then propane-1,3-diamine (3.1 g, 0.042 mol) was added. The mixture was set aside for 24 h at room temperature, then the solvent was removed on a rotary evaporator. The addition of water (10 ml) to the obtained oil caused precipitation of the crude product. Recrystallization from water gave the pure oxime in the form of single crystals. Yield 5.3 g (52%), the purity being checked by elemental analysis, NMR and IR spectroscopy (Calc. for $C_9H_{16}N_4O_4$: C, 44.25; H, 6.62; N, 22.94. Found: C, 44.51; H, 6.67; N, 22.78%). ^1H NMR (270 MHz): δ 1.557 (qnt, 2 H, $^3J = 6.4$, β-CH_2), 1.867 (s, 6 H, CH_3), 3.130 (q, 4 H, $^3J = 6.5$, α-CH_2), 7.975 (t, 2 H, $^3J = 6.1$ Hz, NH) and 11.632 (s br, 2 H, OH). ^{13}C NMR: δ 9.42 (CH_3), 29.23 (β-CH_2), 35.80 (α-CH_2), 150.26 (C=N) and 163.65 (C=O). IR (cm^{-1}): 1024 ν(N–O), 1542 (amide II); 1621 ν(C=O, amide I), 1655 ν(C=N), 2872, 2944, 2965, 2980 ν(C–H), 3214 (br) ν(O–H) and 3345 ν(N–H). Potentiometry also showed the oxime to be almost 100% pure; a very good fit was obtained between calculated and experimental titration curves with alkali over the whole pH range.

Cu(pap)·H$_2$O 1. Copper(II) acetate monohydrate (0.220 g, 1 mmol) dissolved in water (20 ml) was added to a hot aqueous solution (20 ml) of H_2pap (0.244 g, 1 mmol). The mixture was heated at 80–90 °C for 15 min upon stirring and then cooled. The resulting dirty pink precipitate was filtered off, washed with water and acetone and then freeze-dried. Yield 0.20 g (62%). The complex is virtually insoluble in water, dimethyl sulfoxide (dmso) and other common organic solvents (Calc. for $C_9H_{14}CuN_4O_4\cdot H_2O$: C, 33.38; H, 4.98; Cu, 19.63; N, 17.30. Found: C, 33.25; H, 4.92; Cu, 19.40; N, 17.33%). IR (cm^{-1}) 1146 ν(N–O), 1610 (br) ν(C=O, amide I), 2860, 2951, 2974 ν(C–H), 3240 (br) and 3416 (br) ν(O–H).

[Li(H$_2$O)$_4$][Cu(H$_{-1}$pap)]·2H$_2$O 2. To a suspension of complex **1** (0.324 g, 1 mmol) an excess aqueous solution (1.5 ml) of LiOH (2 M) was added. The mixture was stirred at room temperature until complete dissolution of the solid had been reached (*ca.* 10 min). The red-orange solution obtained was filtered and set aside for crystallization at room temperature in a Petri dish. After 48 h clear orange single crystals formed in the solution and were picked for X-ray analysis by hand. In order to isolate the bulky product from Li_2CO_3 after complete drying of the solution, the resulting solid was treated with methanol or acetone (20 ml) and filtered off. Addition of diethyl ether (30 ml) to the filtrate led to precipitation of the complex which was filtered off and air-dried. It is fairly soluble in water, ethanol and acetone (Calc. for $C_9H_{13}CuLiN_4O_4\cdot 6H_2O$: C, 25.74; H, 6.01; Cu, 15.14; N, 13.35. Found: C, 25.61; H, 5.92; Cu, 15.38; N, 13.58%). IR (cm^{-1}): 1110 ν(N–O), 1601 (br) ν(C=O, amide I), 1688 ν(C=N), 2861, 2930, 2972 ν(C–H) and 3320 (br) ν(O–H).

[Ni(H$_2$O)$_6$][Ni(H$_{-1}$pap)]$_2$ 3. An aqueous solution (1.5 ml) of LiOH (2 M) was added to $Ni(NO_3)_2\cdot 6H_2O$ (0.291 g, 1 mmol) dissolved in water (10 ml) upon stirring. The obtained nickel(II) hydroxide was filtered off and washed with water until the resulting filtrate was neutral, the $Ni(OH)_2$ was then suspended in water (10 ml) and added to a hot aqueous solution of H_2pap (0.244 g, 1 mmol). The mixture was heated at 90 °C with continuous stirring for 30 min until a clear yellow solution formed. It was filtered and allowed to cool to room temperature in a porcelain dish with slow evaporation of solvent. In 48–72 h dirty yellow single crystals were formed and isolated by filtration, washed with a small amount of water (2 ml) and dried between sheets of filter paper. The complex is partially soluble in cold water and more so in hot water (Calc. for $C_{18}H_{26}N_8Ni_3O_8\cdot 6H_2O$: C, 28.20; H, 5.01; N, 14.62; Ni, 22.96. Found: C, 27.87; H, 4.86; N, 14.51; Ni, 23.13%). IR (cm^{-1}): 1130 ν(N–O), 1592 (br) ν(C=O, amide I), 2860, 2959 ν(C–H) and 3330 (br) ν(O–H).

Na[Ni(H$_{-1}$pap)]·H$_2$O 4. The synthesis was carried out analogously to that described for complex **3**. After mixing nickel(II) hydroxide with an aqueous solution of H_2pap an excess of an aqueous solution (1.5 ml) of NaOH (2 M) was added. The mixture was stirred for 30 min at 90 °C, filtered and then set aside for evaporation of the solvent at room temperature. The resulting solid was treated with ethanol (30 ml), the insoluble residue was removed by filtration, the solvent from the filtrate was evaporated under reduced pressure. The crude product was recrystallized from isopropyl alcohol–acetone (1 : 1). Complex **4** is fairly soluble in water and ethanol and less so in acetone (Calc. for $C_9H_{13}N_4NaNiO_4\cdot H_2O$: C, 31.70; H, 4.44; N, 16.44; Ni, 17.21. Found: C, 31.35; H, 4.32; N, 16.15; Ni, 17.43%). ^1H NMR (270 MHz): δ 1.337 (m, 2 H, β-CH_2), 1.699 (s, 6 H, CH_3), 2.640 (t, 4 H, $^3J = 5.2$ Hz, α-CH_2), 18.832 (s, 1 H, NOH···ON). IR (cm^{-1}): 1141 ν(N–O), 1585 (br) ν(C=O, amide I), 2852, 2903, 2934, 2959 ν(C–H) and 3438 (br) ν(O–H).

Cu(Hpap)(NO$_3$) 5. The compound $Cu(NO_3)_2\cdot 3H_2O$ (0.121 g, 0.5 mmol) dissolved in ethanol (5 ml) was added to H_2pap (0.122 g, 0.5 mmol) in ethanol (5 ml). In 30 min the green precipitate that had formed was filtered, washed with ethanol and acetone and dried in a vacuum desiccator over $CaCl_2$. The complex is soluble in water and insoluble in methanol and acetone (Calc. for $C_9H_{15}CuN_5O_7$: C, 29.31; H, 4.11; Cu, 17.23; N, 18.99. Found: C, 29.18; H, 4.03; Cu, 17.45; N, 18.68%). IR (cm^{-1}): 1168 ν(N–O), 1390 ν(N–O in NO_3^-), 1588 (amide II), 1632 (br) ν(C=O, amide I), 2860 (sh), 2950 ν(C–H) and 3270 (br) ν(O–H).

Ni(H$_2$pap)(NO$_3$)$_2$ 6. The compound $Ni(NO_3)_2\cdot 6H_2O$ (0.145 g, 0.5 mmol) dissolved in ethanol (5 ml) was added to H_2pap (0.122 g, 0.5 mmol) in ethanol (5 ml). The mixture was allowed to stand at room temperature. After evaporation of the solvent the oily residue was treated with acetonitrile (5 ml), the pale blue solid material that formed was filtered, washed with acetone and dried in a vacuum desiccator over $CaCl_2$. The complex is soluble in water and methanol and insoluble in acetone (Calc. for $C_9H_{16}N_6NiO_{10}$: C, 25.31; H, 3.78; N, 19.69; Ni, 13.74. Found: C, 25.60; H, 3.91; N, 19.50; Ni, 13.80%). IR (cm^{-1}): 1109 ν(N–O), 1388 (br) ν(N–O in NO_3^-), 1561 (amide II), 1620 ν(C=O, amide I), 1673 ν(C=N), 2881, 2972 ν(C–H) and 3320 (br) ν(O–H).

Potentiometric studies

Titrations involved an ionic background of 0.1 mol dm^{-3} KNO_3, a ligand concentration of 2×10^{-3} mol dm^{-3} and metal-to-ligand molar ratios of 1 : 1, 1 : 2 and 1 : 5. Stability constants for the complexes of H^+, Cu^{2+} and Ni^{2+} were calculated from titrations carried out using total volumes of 2 cm^3 only for data sets of 1 : 5 metal-to-ligand molar ratios as in the other cases precipitation of solid occurs at pH 4.5–6.5. Alkali was added from a 0.250 cm^3 micrometer syringe which had been calibrated by weight titrations and titration of standard materials. The pH-metric titrations were performed at 25 °C using a MOLSPIN automatic titration system with a microcombined glass–calomel electrode calibrated daily in hydrogen-ion concentration using HNO_3.[10] Titrations were performed in triplicate and the SUPERQUAD computer program was used for calculations of stability constants ($\beta_{pqr} = [M_pH_rL_q]/[M]^p[H]^r[L]^q$).[11] Standard deviations quoted refer to random errors only. They are, however, a good indication of the importance of a particular species in the equilibrium. The results of the solution study are presented in Table 1.

Spectroscopic studies

Absorption spectra were recorded on a Beckman DU 650 spectrophotometer. The metal-ion concentrations were 3×10^{-3} mol dm^{-3} and metal-to-ligand molar ratios were 1 : 1, 1 : 2 and 1 : 5. The UV/VIS measurements of diffuse-reflectance spectra were made on a Beckman UV 5240 spectrometer. The EPR spectra were recorded on a Brüker ESP 300E spectrometer at X-band (9.3 GHz) at 120 K, in ethane-1,2-diol–water (1 : 2). Concentrations used in the spectroscopic measurements were similar to those given for potentiometric titrations. Infrared spectra (KBr pellets) have been recorded on a Perkin-Elmer 180 Spectrometer in the range of 400–4000 cm^{-1}. Proton and ^{13}C NMR spectra have been obtained on a Brüker apparatus (300 MHz) and on a JEOL EX apparatus (270 MHz) in [$^2H_6$]dmso using $SiMe_4$ as an internal standard. Chemical shifts δ are given in ppm downfield from the reference. The results of the UV/VIS and EPR spectroscopy studies of the synthesised compounds are given in Table 2.

Crystallography

Details of the crystal data and refinement for the compounds studied are given in Table 3. The accurate unit-cell parameters and the orientation matrices were calculated using the least-squares technique. Intensities were collected using a KUMA KM4 diffractometer in the ω–2θ scan mode. The intensities of three standard reflections, monitored every 100 intensity scans showed no evidence of crystal decay. Corrections for Lorentz and polarisation effects but not for absorption were applied. All structures were solved by direct methods using SHELXS 86[12] and refined by full-matrix, least squares on F_o^2 using SHELXL 93.[13] Neutral atom scattering factors and anomalous dispersion terms used in the refinement were taken from ref. 14, real and imaginary components of anomalous dispersions were included for all non-H atoms. The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms in H_2pap were localized from a Fourier-difference map and their positional and isotropic displacement parameters were included in the final stage of the refinement. In complexes **2** and **3** the O–H and N–H hydrogen atoms were found on the Fourier-difference map but were not included in the refinement, the location of the C–H atoms of methyl and methylene groups was set in calculated positions and allowed to ride on the atoms to which they were linked.

CCDC reference number 186/679.

Table 1 Spectroscopic (UV/VIS and EPR) and potentiometric data for Cu^{2+}–pap and Ni^{2+}–pap systems in the molar ratio metal-to-ligand 1 : 5, at 25 °C and $I = 0.1$ M KNO_3

Species							
M	H	L	log β	λ_{max}/nm	ε/M^{-1} cm^{-1}	$A_\parallel$/G	$g_\parallel$
0	1	1	10.383(9)				
0	2	1	19.993(7)				
Cu^{2+} complexes							
1	1	1	19.61(4)	620	85[a]	178	2.244
1	−1	1	9.95(4)	470	105[a]	213	2.164
1	−2	1	2.08(8)	479	121[a]	210	2.164
Ni^{2+} complexes							
1	−1	1	1.14(9)	301 (sh)	1931[b]		
				369	4573[b]		
				399 (sh)	1906[b]		
				441	439[a]		
1	−2	1	−7.05(11)	369	4585[b]		
				399 (sh)	1962[b]		
				441	437[a]		

[a] d–d Transitions. [b] Charge-transfer transitions.

Results and Discussion

Solution studies

The compound H_2pap exhibits two measurable dissociation constants corresponding to stepwise deprotonation of two hydroxyimino groups [pK_{a1} = 9.61(7) and pK_{a2} = 10.38(4)]. The first value is close to that determined for Hpox (pK = 9.87[1]). The observed values of the protonation constants are on average 1–3 orders lower than those reported for 1,2-dioximes {*e.g.* pK_a = 12.9 reported for dimethylglyoxime [$CH_3C(=NOH)$-$C(=NOH)CH_3$][15]} which may be explained in terms of electron-withdrawing effects of the amide groups in the α-positions.

The complex species evaluated from the potentiometric calculations for Cu^{2+} and Ni^{2+} are presented in Table 1. The species $[MH_{-1}L]^-$ and $[MH_{-2}L]^{2-}$ were found to be dominant over wide ranges of pH both in Cu^{2+} (above pH 4) and Ni^{2+} (above pH 7) systems (Fig. 1). Formation of the first species is

Table 2 Absorption spectra of the synthesised compounds

Compound	Solution spectra	UV/VIS absorption bands λ/nm[a] (ε/M^{-1} cm^{-1})	Reflectance bands/nm
H_2pap	Water	237 (7740)[b] 208 (7740)[b]	
1 $Cu(pap)\cdot H_2O$	Water		526 364[c]
2 $[Li(H_2O)_4][Cu(H_{-1}pap)]\cdot 2H_2O$	Water	479 (136) (pH 8)	460 338[c]
3 $[Ni(H_2O)_6][Ni(H_{-1}pap)]_2$	Water	295 (sh) (6028) 375 (1198) 400 (sh) (580) 556 (12.6) 665 (sh) (0.47) 740 (0.5)	409 (sh) 645 (sh) 725
4 $Na[Ni(H_{-1}pap)]\cdot H_2O$	Water	293 (sh) 368 400 (sh)	408 (sh)
5 $Cu(Hpap)(NO_3)$	Water	695 (99) (pH 4)	366[c] 611
6 $Ni(H_2pap)(NO_3)_2$	Water	398 (46) 368 (111)[c] (pH 5.05)	365 (sh) 382 627 760 (sh)
	Ethanol	390 (24) 671 (6.7) 744 (6.4)	

[a] d–d Transition except where indicated otherwise. [b] Intraligand transition. [c] Charge transfer.

Table 3 Crystal data and structure refinement for H_2pap, complexes **2** and **3**[a]

	H_2pap	$[Li(H_2O)_4][Cu(H_{-1}pap)]\cdot 2H_2O$ **2**	$[Ni(H_2O)_6][Ni(H_{-1}pap)]_2$ **3**
Empirical formula	$C_9H_{16}N_4O_4$	$C_9H_{25}CuLiN_4O_{10}$	$C_{18}H_{38}N_8Ni_3O_{14}$
M	244.26	419.81	766.70
Space group	$P2_1/c$	$P2_1/n$	$C2/c$
a/Å	9.559(2)	7.1790(10)	15.847(3)
b/Å	14.477(3)	27.647(6)	11.518(2)
c/Å	8.376(2)	8.824(2)	15.382(3)
β/°	90.37(3)	94.50(3)	99.21(3)
U/Å^3	1159.1(4)	1746.0(6)	2771.4(9)
D_c/Mg m^{-3}	1.400	1.597	1.838
μ/cm^{-1}	1.11	13.07	21.00
F(000)	520	876	1592
Crystal size/mm	0.20 × 0.25 × 0.30	0.20 × 0.25 × 0.25	0.15 × 0.15 × 0.18
θ Range/°	2.13–25.06	2.4–25.05	2.2–25.05
Range hkl	−11 to 11, −17 to 0, 0–9	0–8, 0–32, −10 to 10	0–12, 0–13, −18 to 18
Reflections collected	2189	3060	2145
Data, parameters	1194, 218	1840, 230	1273, 197
Goodness of fit on F^2	1.031	1.119	1.131
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0319, 0.0828	0.0407, 0.1068	0.0313, 0.0790
Maximum, minimum electron density/e Å^{-3}	0.204, −0.181	0.562, −0.790	0.400, −0.379

[a] Details in common: crystal system monoclinic, wavelength 0.710 69 Å, $T = 293(2)$ K and $Z = 4$. [b] $R1 = \Sigma(F_o - F_c)/\Sigma F_o$. $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ where $w = 1/\sigma^2(F_o^2) + (0.0496\ P)^2 + 0.2573\ P$ for H_2pap, $1/\sigma^2(F_o^2) + (0.0629\ P)^2 + 3.4900\ P$ for **2** and $1/\sigma^2(F_o^2) + (0.0599\ P)^2$ for **3** where P is defined as $(F_o^2 + 2F_c^2)/3$.

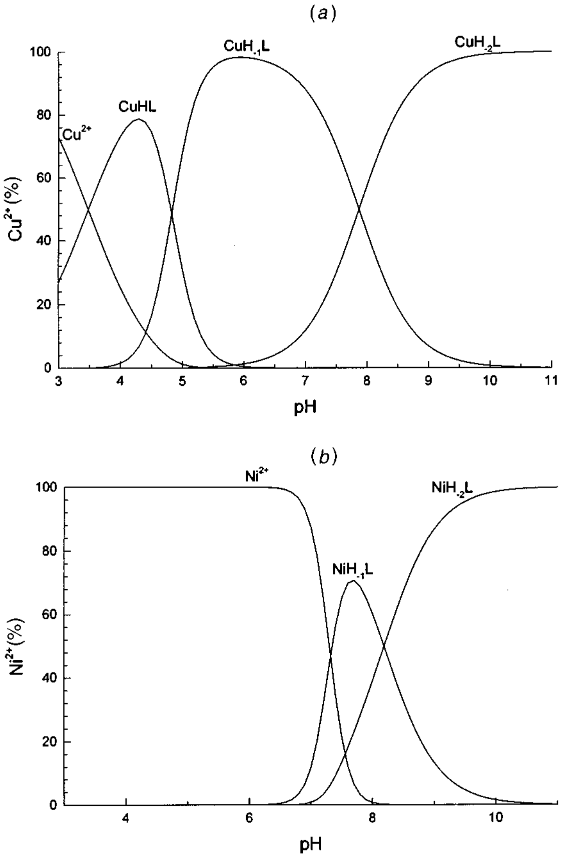


Fig. 1 Species distribution diagram for Cu^{II}–pap (a) and Ni^{II}–pap systems (b) at 25 °C and $I = 0.1$ M. Concentration of ligand 0.005 and concentration of metal ions 0.001 M

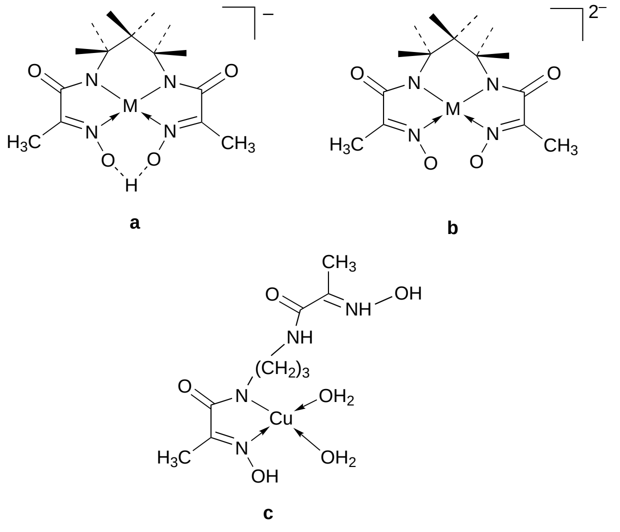


Fig. 2 Suggested structures for $[MH_{-1}L]^-$ in complexes **2**–**4** **a**, $[MH_{-2}L]^{2-}$ **b** and $[CuHL]^+$ in solution **c**

certainly connected with the effect of stabilization of the square planar MN_4 co-ordination due to the presence of three fused chelate rings (Fig. 2, **a**). The additional stabilization is achieved because of the short intramolecular hydrogen-bond between *cis*-situated oxime oxygen atoms which is typical for bis(oximato) complexes. Thus, the co-ordination can be described as pseudo-macrocyclic. This is confirmed by the two crystal-structure studies described below. It is interesting to note that the stability constant of the $CuH_{-1}L$ complex is more than 8 orders of magnitude higher than that of the $NiH_{-1}L$ species (Table 1). In the case of simple chelates with the same binding mode, *e.g.* for 2-(hydroxyimino)propanamide, the stability constants differ by only around 4 orders of magnitude.[1] The large differences in stability constants with H_2pap may also be attributable to the differences in the ionic radii. Larger Cu^{II} ions may fit better to the ligand binding site than those of Ni^{II}.

The complexes $[MH_{-2}L]^{2-}$ start to be formed at higher pH, the corresponding pK_a($[MH_{-1}L]^-$) values (7.87 for Cu^{2+} and 8.18 for Ni^{2+}) suggest deprotonation of the second oxime group. In both cases deprotonation is easier by one order of magnitude when compared to the pK_{a1} of H_2pap. It is worthy to note that the pK_a values corresponding to the loss of the oxime bridging proton in the Cu^{2+} complex with the simple Hpox ligand is 10.40 and in the Ni^{2+} complexes with Hpox and oximes of *N*-pyruvoylglycine and *N*-pyruvoyl-L-alanine these values are 10.54, 11.20 and 11.07, respectively.[1,2] These latter values are somewhat higher than deprotonation constants of the metal-free ligands. This indicates that the loss of the bridging oxime proton in the present cases proceeds more easily than in the simple bidentate ligands. In the absorption spectra of Cu^{2+} systems only one maximum is observed in the visible region at pH 5.5 and higher (479 nm) that is close to the values

Table 4 Selected bond lengths (Å) and angles (°) for H_2pap

O(1)–N(1)	1.390(2)	N(2′)–C(3′)	1.330(3)
O(1′)–N(1′)	1.388(2)	N(2′)–C(4′)	1.446(3)
O(2)–C(3)	1.230(2)	C(1)–C(2)	1.481(3)
O(2′)–C(3′)	1.236(2)	C(1′)–C(2′)	1.484(3)
N(1)–C(2)	1.274(2)	C(2)–C(3)	1.495(3)
N(1′)–C(2′)	1.277(2)	C(2′)–C(3′)	1.491(3)
N(2)–C(3)	1.322(3)	C(4)–C(5)	1.504(3)
N(2)–C(4)	1.455(3)	C(4′)–C(5)	1.516(3)
C(2)–N(1)–O(1)	112.1(2)	O(2)–C(3)–N(2)	121.9(2)
C(2′)–N(1′)–O(1′)	111.6(2)	O(2)–C(3)–C(2)	120.5(2)
C(3)–N(2)–C(4)	122.5(2)	N(2)–C(3)–C(2)	117.6(2)
C(3′)–N(2′)–C(4′)	123.1(2)	O(2′)–C(3′)–N(2′)	123.5(2)
N(1)–C(2)–C(1)	125.9(2)	O(2′)–C(3′)–C(2′)	119.9(2)
N(1)–C(2)–C(3)	115.9(2)	N(2′)–C(3′)–C(2′)	116.6(2)
C(1)–C(2)–C(3)	118.8(2)	N(2)–C(4)–C(5)	110.5(2)
N(1′)–C(2′)–C(1′)	126.7(2)	N(2′)–C(4′)–C(5)	112.3(2)
N(1′)–C(2′)–C(3′)	114.2(2)	C(4)–C(5)–C(4′)	113.6(2)
C(1′)–C(2′)–C(3′)	119.0(2)		

reported for tetraazamacrocyclic complexes.[16] The Ni^{2+} systems above pH 7.0 display the absorption bands typical for square-planar complexes [369 and 399 (sh) nm]. This clearly indicates the presence of an MN_4 species. The positions of the absorption maxima are noticeably shifted towards higher energies as compared to the spectra of Hpox complexes (613 and 505 nm for $[CuH_{-1}L_2]^-$ and $[CuH_{-2}L_2]^{2-}$; 405 and 408 nm for $[NiH_{-1}L_2]^-$ and $[NiH_{-2}L_2]^{2-}$ species, respectively).[1,2] These shifts in the d–d transition energies can derive from the triple chelate and pseudo-macrocyclic effects. The positions of absorption maxima reported for the complexes with 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime indicate a similar pseudo-macrocyclic co-ordination mode with short intramolecular H-bonds, however, they are centered at longer wavelengths (520 nm for Cu^{2+} [17] and 423 nm for Ni^{2+} complexes [18]). These differences derive from the weaker ligand field contributions of two amine groups compared with two deprotonated amide nitrogens in H_2pap complexes.[19] There is no d–d transition energy shift upon formation of $[MH_{-2}L]^{2-}$ after deprotonation of the oxime proton in $[MH_{-1}(HL)]$ species. This means that the stabilization of the square-planar geometry in H_2pap complexes is determined mostly by the presence of three fused chelate rings, and the H-bond plays a less significant role as in the cases of other oxime ligands mentioned above.

In the Cu^{2+}–H_2pap system the $[CuHL]^+$ complex is also detected (Table 1). It dominates in the range pH 3.5–4.5. In the UV/VIS spectra the absorption band at 620 nm can be ascribed to this complex which is expected to have two nitrogen and two oxygen atoms bound in equatorial positions with one of the amide groups being deprotonated (Fig. 2, **c**). Similar d–d transition energies in the absorption spectra for complex species with the same {N_{oxime}, N_{amide}, 2O} co-ordination mode were observed in systems with Hpox (688 nm) and *N*-pyruvoylglycine oxime (666 nm).[1] The difference between logβ($[CuHL]^+$) and logβ($[CuH_{-1}L]^-$) (9.66) corresponds to the loss of two protons belonging to the amide and oxime groups. This is less than half the sum of pK_a values typical for deprotonation of amide and oxime groups in Cu^{2+} complexes which indicates the critical impact of pseudo-macrocyclic co-ordination on the stabilization of the co-ordination sphere in the complexes studied here.

Solid-state X-ray studies

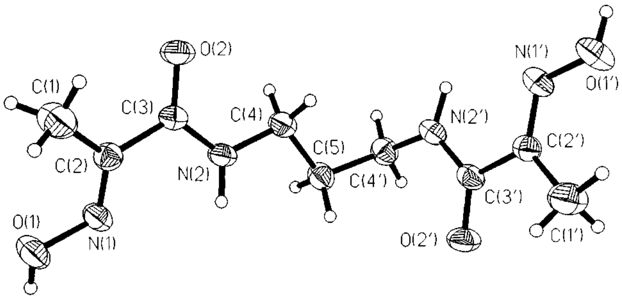


Fig. 3 Molecular structure of H_2pap

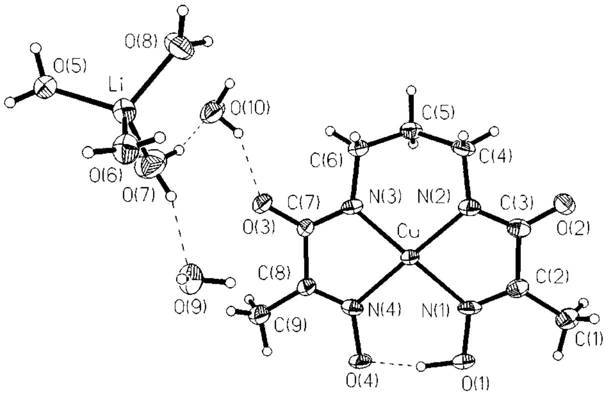


Fig. 4 Structure and numbering scheme for complex **2**

The view of the H_2pap molecule is presented in Fig. 3 and selected bond distances and angles are in Table 4. One can see that the 'free' molecule is in an elongated conformation approaching linearity. The molecule consists of two nearly planar $CH_3C(=NOH)C(O)NHCH_2$ fragments linked by a methylene group. This conformation is the same as that observed in the structures of Hpox and *N*-pyruvoylamino acid oximes: the oxime group is in a *trans* position with respect to the amide carbonyl, the amide bonds indicate a *trans* configuration. Note that both moieties deviate somewhat from planarity because of a slight twisting of the oxime and amide groups along the C(2)–C(3) and C(2′)–C(3′) bonds which is similar to the molecule structure of Hpox.[20] In contrast, the structure studies of pyruvoylamino acid oximes,[21] the anionic complexes of cobalt(III) with pyruvoylglycine oxime[22] and nickel(II)[2] and copper(II)[23] complexes with Hpox revealed these moieties to be nearly planar. The conformationally flexible fragment $(CH_2)_3$ lies nearly in the plane of the amide group [O(2)C(3)N(2)C(4)] [torsion angles C(3)–N(2)–C(4)–C(5) = −176.2(2)° and N(2)–C(4)–C(5)–C(4′) = −171.9(2)°], so that the molecule consists of two relatively planar moieties with a common C(4′) atom. The dihedral angle between the corresponding least square planes is 96.2°. The bond lengths and angles of the molecule are normal for oxime- and amide-containing compounds.

Both structures of complexes **2** and **3** are ionic and consist of complex anions $[M(H_{-1}pap)]^-$ (M = Cu or Ni) and counter ions, $[Li(H_2O)_4]^+$ in complex **2** and $[Ni(H_2O)_6]^{2+}$ in complex **3**. In the unit cell of **2** there are two solvent water molecules as well. Both co-ordinated and solvent water molecules in **2** and **3** form extensive systems of multibranched hydrogen-bonds uniting the elements of the structures between each other. The view of the molecules and the numbering schemes for **2** and **3** are represented in Figs. 4 and 5, respectively. Selected bond lengths and angles for **2** and **3** are shown in Table 5. The ligand in the complex anions is co-ordinated in a tetradentate fashion, forming three condensed chelate rings and being triply deprotonated. The co-ordination sphere is planar, formed by four nitrogen atoms belonging to the deprotonated amide and hydroxyimino groups, subject to slight tetrahedral distortions. The latter are minimal in **3** and more noticeable in **2**: the deviations of the metal and donor atoms from the N(1)N(2)-N(3)N(4) plane in **3** do not exceed 0.02 Å while in **2** the nitrogen atoms lie 0.028 Å alternatively above or below the mean plane, and the copper atom is displaced 0.077 Å in the direction of the axial donor atom N(2) of the neighbouring molecule. Note, that the Ni(1) atom in **4** has a remote contact with the O(5) (0.5 − *x*, −0.5 + *y*, 1.5 − *z*) atom of the water molecule with Ni–O 2.901(3) Å. The Ni–N bond distances in **3** coincide

Table 5 Selected bond lengths (Å) and angles (°) for complexes **2** and **3**

Co-ordination polyhedra

Complex **2**

Cu–N(1)	1.962(4)	Cu–N(4)	1.954(4)
Cu–N(2)	1.927(4)	Cu–N(2^{I})	3.097(4)
Cu–N(3)	1.910(4)	Cu $\cdots$ Cu^{I}	3.504(2)

N(3)–Cu–N(2)	98.6(2)	N(3)–Cu–N(1)	173.8(2)
N(3)–Cu–N(4)	82.7(2)	N(2)–Cu–N(1)	81.6(2)
N(2)–Cu–N(4)	176.8(2)	N(4)–Cu–N(1)	96.8(2)

Complex **3**

Ni(1)–N(1)	1.865(3)	Ni(1)–N(4)	1.865(3)
Ni(1)–N(2)	1.864(3)	Ni(1)–O(5^{II})	2.901(3)
Ni(1)–N(3)	1.869(3)	Ni(1) $\cdots$ Ni(1^{III})	3.812(1)

N(1)–Ni(1)–N(2)	82.4(2)	N(4)–Ni(1)–N(3)	82.5(2)
N(1)–Ni(1)–N(4)	97.44(14)	N(1)–Ni(1)–O(5^{II})	84.70(11)
N(2)–Ni(1)–N(4)	178.6(2)	N(2)–Ni(1)–O(5^{II})	95.24(13)
N(1)–Ni(1)–N(3)	179.22(14)	N(4)–Ni(1)–O(5^{II})	86.14(12)
N(2)–Ni(1)–N(3)	97.6(2)	N(3)–Ni(1)–O(5^{II})	96.07(12)

Ligands

	Complex **2**	Complex **3**
O(1)–N(1)	1.380(5)	1.370(4)
O(2)–C(3)	1.246(6)	1.257(5)
O(3)–C(7)	1.258(6)	1.266(5)
O(4)–N(4)	1.362(5)	1.354(4)
N(1)–C(2)	1.272(7)	1.278(5)
N(2)–C(3)	1.319(7)	1.312(5)
N(2)–C(4)	1.456(6)	1.467(5)
N(3)–C(7)	1.312(7)	1.299(5)
N(3)–C(6)	1.455(6)	1.459(5)
N(4)–C(8)	1.276(6)	1.270(5)
C(1)–C(2)	1.471(7)	1.482(5)
C(2)–C(3)	1.524(7)	1.486(6)
C(4)–C(5)	1.525(7)	1.504(6)
C(5)–C(6)	1.497(8)	1.525(6)
C(7)–C(8)	1.513(7)	1.497(6)
C(8)–C(9)	1.470(7)	1.486(5)
C(2)–N(1)–O(1)	118.5(4)	118.8(3)
C(3)–N(2)–C(4)	119.4(4)	118.6(3)
C(7)–N(3)–C(6)	121.2(4)	118.5(3)
C(8)–N(4)–O(4)	121.2(4)	118.9(3)
N(1)–C(2)–C(1)	124.8(5)	123.8(4)
N(1)–C(2)–C(3)	113.0(5)	111.7(4)
C(1)–C(2)–C(3)	122.2(5)	124.5(4)
O(2)–C(3)–N(2)	127.9(5)	127.2(4)
O(2)–C(3)–C(2)	118.9(5)	120.5(4)
N(2)–C(3)–C(2)	113.2(5)	112.2(4)
N(2)–C(4)–C(5)	111.4(4)	110.9(4)
C(6)–C(5)–C(4)	117.6(4)	113.5(4)
N(3)–C(6)–C(5)	111.8(4)	110.5(4)
O(3)–C(7)–N(3)	126.6(5)	127.3(4)
O(3)–C(7)–C(8)	118.8(5)	120.1(4)
N(3)–C(7)–C(8)	114.6(4)	112.6(4)
N(4)–C(8)–C(9)	126.3(5)	125.7(4)
N(4)–C(8)–C(7)	112.7(4)	111.5(4)
C(9)–C(8)–C(7)	121.0(4)	122.8(4)

Symmetry transformations used to generate equivalent atoms I: $-x + 1, -y, -z$, II: $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ and III: $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

[1.864(3)–1.869(4) Å], while the Cu–N distances in **2** are considerably longer, the Cu–N (amide) bonds [Cu–N(2) 1.927(4) and Cu–N(3) 1.910(4) Å] are noticeably longer than the Cu–N (oxime) ones [Cu–N(1) 1.962(4) and Cu–N(4) 1.954(4) Å]. The observed bond lengths are typical for nickel(II) and copper(II) oximato and amidato square planar complexes; very similar parameters were seen in the structures of the complexes with Hpox.[2,23] The bite angles N(1)–M–N(2) and N(3)–M–N(4) in the five-membered rings are decreased to 81.6(2) and 82.7(2)° in **2** and to 82.4(2) and 82.6(2)° in **3**, respectively from free H_2pap.

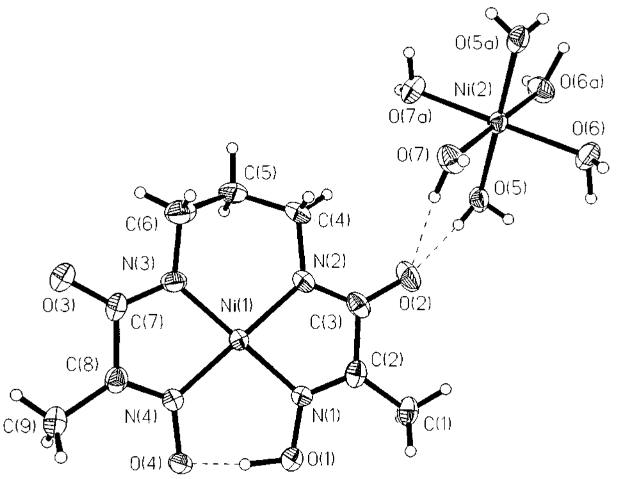


Fig. 5 Structure and numbering scheme for complex **3**

In contrast, the N(2)–M–N(3) angles in the six-membered chelate rings are increased to 98.6(2)° in **2** and 97.6(2)° in **3**.

The six-membered chelate rings MN(2)C(4)C(5)C(6)N(3) indicate exactly an envelope conformation which is dictated by the requirement to retain planarity of the amide groups upon proton substitution and chelate formation. The C(5) atoms are situated 0.664 and 0.718 Å away from the plane N(2)N(3)-C(4)C(6) in **2** and **3**, respectively; the corresponding dihedral angles along C(4)–C(6) line are equal to 122.0 and 120.2°, respectively. The five-membered chelates MN(1)C(2)C(3)N(2) and MN(3)C(7)C(8)N(4) in both structures are nearly planar, the deviations of the atoms from the least-square planes do not exceed 0.02 Å.

Earlier we concluded that the short intramolecular hydrogen-bond between oxime oxygen atoms which is peculiar for oximato complexes implies a *cis* configuration of the co-ordination sphere in nickel(II) and copper(II) complexes with Hpox and *N*-pyruvoylamino acid oximes.[1,2,23] In complexes **2** and **3** these bonds additionally stabilize the co-ordination sphere thus leading to its pseudo-macrocyclic configuration. In both cases the bridging proton is localized near the O(1) atoms and the short H-bonds are asymmetric [in **2**: O(1)–H 1.087(4), H $\cdots$ O(4) 1.534(4), O(1) $\cdots$ O(4) 2.581(5) Å, O(1)–H $\cdots$ O(4) 160.1(2)°; in **3**: O(1)–H 1.030(3), H $\cdots$ O(4) 1.413(3), O(1) $\cdots$ O(4) 2.436(4) Å, O(1)–H $\cdots$ O(4) 171.7(3)°]. It is evident that the reason for this asymmetry is hydrogen-bonding of the O(4) oxygen atoms in both structures with the water molecules. The considerable difference in the O(1) $\cdots$ O(4) separation in **2** and **3** is probably connected with the short Ni–N bond distances as compared to Cu–N distances resulting in a closer arrangement of oxime oxygen atoms in **3**.

Upon co-ordination the ligands undergo rather insignificant changes in the geometrical parameters. The small shortening of the N–O distances in the hydroxyimino groups and C–N distances as well as elongation of the C=O bonds in the amide groups are characteristic of oxime and amide donor ligands and were observed earlier in the relevant structures.[22,24] At the same time the conformation of the co-ordinated ligand in **2** and **3** differs significantly from that found in the free ligand. In the latter case it is rather linear, while in the complexes it is rather cyclic. Such changes are possibly due to the presence of the conformationally flexible trimethylene moiety.

The relatively rigid fragments $CH_3C(=NOH)C(O)NHCH_2$ in **2** and **3** are much closer to pure planar geometry than those found in H_2pap. The values of the torsion angles within the mentioned fragment in **2** and **3** are inclined no more than 7° from values of 0 or 180° while in the free ligand these deviations reach 23°.

The square-planar co-ordination of the central ion in **2** is approaching distorted square pyramidal on account of an elongated Cu–N(2) [3.097(4) Å] axial contact with the amide nitrogen atom belonging to the neighbouring molecule related by the symmetry operation $1 - x, -y, -z$. Thus, the copper(II) complex anions form centrosymmetric dimers with Cu···Cu distances of 3.504(2) Å. The translational dimers are packed in the linear columns along the x axis, the Cu···Cu separations between dimers are 4.120(2) Å. The insertion of chains consisting of $[Li(H_2O)_4]^+$ cations lying parallel to the x direction unite the translational complex anion columns into the crystal structure on account of hydrogen bonds.

In complex **3** the complex anions are arranged in a parallel fashion forming pairs related by the centre of symmetry at the point $(\frac{1}{4}\ \frac{1}{4}\ \frac{1}{2})$ with Ni···Ni separations of 3.812(1) Å and Ni···N(1) of 3.446(3) Å $(0.5 - x, 0.5 - y, 1 - z)$ which is normal for packing of nickel(II) square-planar complexes. The $[Ni(H_2O)_6]^{2+}$ octahedra link the translational complex anions in the x and y directions *via* hydrogen bonds formed by the coordinated water molecules with the amide and oxime oxygen donor atoms of the complex anions, thus each cation seems to be linked with six complex anions.

Conclusion

Open chain oximes co-ordinating to metal ions *via* two oxime and two amide nitrogens are shown to be very effective ligands for Ni^{II} and Cu^{II} ions. It seems that amide nitrogens have a strong impact on binding abilities, while the hydrogen bond between two oxime oxygens is less important than that in simple oximes. However, the presence of the hydrogen bonds close the open chain structure into the closed macrocyclic system.

Acknowledgements

This work was supported by a grant from the Polish State Committee for Scientific Research and University of Wrocław. I. O. F. and T. Yu. S. thank the Kasa im. J. Mianowskiego Foundation for Scholarships.

References

1 C. O. Onindo, T. Yu. Sliva, T. Kowalik-Jankowska, I. O. Fritsky, P. Buglyo, L. D. Pettit, H. Kozłowski and T. Kiss, *J. Chem. Soc., Dalton Trans.*, 1995, 3911.
2 T. Yu. Sliva, T. Kowalik-Jankowska, V. M. Amirkhanov, T. Głowiak, C. O. Onindo, I. O. Fritsky and H. Kozłowski, *J. Inorg. Biochem.*, 1997, **65**, 287.
3 B. Kurzak, H. Kozłowski and E. Farkas, *Coord. Chem. Rev.*, 1992, **114**, 169.
4 V. Yu. Kukushkin, D. Tudela and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 1996, **156**, 333.
5 R. Ruiz, J. Sanz, B. Cervera, F. Lloret, M. Julve, C. Bois, J. Faus and M. Carmen Munoz, *J. Chem. Soc., Dalton Trans.*, 1993, 1623.
6 D. Mansuy, P. Battioni and J.-P. Battioni, *Eur. J. Biochem.*, 1989, **184**, 267; B. Meunier, *Chem. Rev.*, 1991, **92**, 1411.
7 J. Custot, J.-L. Boucher, S. Vadon, C. Guedes, S. Dijols, M. Delaforge and D. Mansuy, *J. Biol. Inorg. Chem.*, 1995, **1**, 73.
8 T. Yu. Sliva, A. M. Duda, T. Głowiak, I. O. Fritsky, V. M. Amirkhanov, A. A. Mokhir and H. Kozłowski, *J. Chem. Soc., Dalton Trans.*, 1997, 273.
9 H.-P. Lau and C. D. Gutsche, *J. Am. Chem. Soc.*, 1978, **100**, 1857.
10 H. M. Irving, M. H. Miles and K. D. Pettit, *Anal. Chim. Acta*, 1967, **68**, 475.
11 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.
12 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
13 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.
14 *International Tables for Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
15 R. Charles and H. Freuer, *Anal. Chim. Acta*, 1954, **11**, 101.
16 Ya. D. Lampeka, A. V. Perikhod'ko, A. Yu. Nazarenko and E. B. Rusanov, *J. Chem. Soc., Dalton Trans.*, 1996, 2017; I. F. Maloshtan and Ya. D. Lampeka, *Zh. Neorg. Khim., 1996,* **41**, 1845.
17 G. E. Jackson and B. S. Nakani, *J. Chem. Soc., Dalton Trans.*, 1996, 1373.
18 M. S. Hussain and E. O. Schlemper, *Inorg. Chem.*, 1979, **18**, 2275.
19 H. Sigel and R. B. Martin, *Chem. Rev.*, 1982, **82**, 385.
20 Yu. A. Simonov, A. A. Dvorkin, T. I. Malinowsky, E. E. Gubina, R. D. Lampeka and I. O. Fritsky, *Izv. Akad. Nauk Mold. SSR, Ser. Biol. Chim. Nauk*, 1992, **1**, 16.
21 R. D. Lampeka, A. A. Dvorkin, Yu. A. Simonov, I. O. Fritsky and V. V. Skopenko, *Ukr. Khim. Zh.* (*Russ. Edition*), 1989, **55**, 458; A. A. Dvorkin, I. O. Fritsky, Yu. A. Simonov, R. D. Lampeka, M. D. Mazus and T. I. Malinowsky, *Dokl. Akad. Nauk SSSR*, 1990, **310**, 87; A. A. Dvorkin, Yu. A. Simonov, V. V. Skopenko, I. O. Fritsky and R. D. Lampeka, *Dokl. Akad. Nauk. SSSR*, 1990, **313**, 98; V. Kh. Kravtsov, O. N. Rebrova, Yu. A. Simonov, R. D. Lampeka and I. O. Fritskii, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1992, **37**, 743.
22 I. O. Fritsky, R. D. Lampeka, V. V. Skopenko, Yu. A. Simonov, A. A. Dvorkin and T. I. Malinowsky, *Z. Naturforsch., Teil B*, 1993, **48**, 270.
23 Yu. A. Simonov, V. Kh. Kravtsov, I O Fritskii, E. E. Gubina, R. D. Lampeka, T. S. Iskenderov and A. Zh. Zhumabaev, *Koord. Khim.*, 1995, **21**, 407.
24 I. O. Fritsky, R. D. Lampeka, V. Kh. Kravtsov and Yu. A. Simonov, *Acta Crystallogr., Sect. C*, 1993, **49**, 1041; I. O. Fritsky, R. D. Lampeka, V. V. Skopenko, Yu. A. Simonov and A. A. Dvorkin, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1994, **39**, 771.

Received 9*th May* 1997; *Paper* 7/03202A