19. Synthesis and Complexation of 1,2-Bis[(monoaza[15]crown-5)-*N*-yl]glyoxime. Crystal Structure of (1,2-Bis[(monoaza[15]crown-5)-*N*-yl]glyoximato)palladium(II)

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A new vicinal dioxime ligand with two crown-ether groups, 1,2-bis[(monoaza[15]crown-5)-*N*-yl]-glyoxime(LH_2), has been prepared from cyanogen di-*N*-oxide and monoaza[15]crown-5. Ni(II), Pd(II), and Pt(IV) complexes of LH_2 with or without alkali-metal ions bound to macrocyclic groups have been isolated. The high affinity of $[Pd(LH)_2]$ and $[Ni(LH)_2]$ for the K^+ ion is observed in solvent extraction experiments. A single-crystal X-ray structure confirms the postulated geometry of $[Pd(LH)_2]$. The Pd-atom of the centro-symmetric molecule has square-planar PdN_4 coordination where Pd–N distances range from 1.978(3) to 1.970(3) Å. The N–Pd–N intraligand angle is 79.9(1)°.

Introduction. – Vicinal dioximes have received considerable attention as model compounds to mimic biofunction such as reduction of vitamin B_{12} [1] [2]. Their complexes have been the source, through the decades, of a never-ending series of interesting reports.

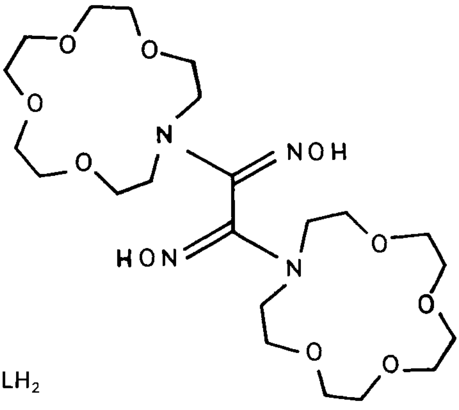
Although extensively investigated under the tacit assumption of their bidentate involvement in metal-ion coordination, most studies are mainly based on spectroscopic evidence [3] [4], only relatively few X-ray data are available [5–7]. In the Co(II) complex of diaminoglyoxime ($NH_2C(=NOH)C(=NOH)NH_2$), the Co-atom has a square-pyramidal coordination with the 4 oxime N-atoms of two chelating diaminoglyoxime molecules at the basis and amino N-atoms of adjacent complexes at the apexes, thus forming sort of chains in the lattice [5]. When this Co(II) complex was crystallized from HCl solution, tris(diaminoglyoxime)cobalt(III) trichloride was formed, with the Co(III) atoms octahedrally coordinated by the bidentate ligand [6].

The reaction of amines or thiols with (*E*,*E*)-dichloroglyoxime or cyanogen di-*N*-oxide yielded various symmetrically substituted diaminoglyoxime or dithioglyoxime derivatives [8–11]. The (*E*,*E*)- and (*E*,*Z*)-stereoisomers of vicinal dioximes are capable of coordinating through N,N or N,O sites of the oxime groups, and only in a few cases it is possible to realize the interconversion of (*E*,*E*)- and (*E*,*Z*)-complexes [9]. In the case of

(*E*,*E*)-monochloroglyoxime, asymmetric vicinal dioximes have been obtained. The transition-metal complexes of these vicinal dioximes are essentially *N*,*N*-coordinated square-planar structures, but the uranyl complexes form *μ*-hydroxo-bridged dimers with *N*,*O*-coordination as shown by IR and ^{1}H-NMR spectra [12].

Other types of vicinal dioxime complexes which have been investigated and compared with dimethylglyoximato analogs are transition-metal complexes of 5,6-dihydrocyclopent[*f*,*g*]acenaphthylene-1,2-dione dioxime and acenaphthylene-1,2-dione dioxime [13] [14]. We have also initiated studies on transition-metal complexes of vicinal dioximes incorporating macrocyclic groups which are capable of binding transition- and alkali-metal ions simultaneously. Thus, we have synthesized new ligands containing substituted benzo[15]crown-5 groups in addition to the vicinal-dioxime moiety [12] [15] [16] which allow alkali-metal binding and enhance the solubility of the complexes in various solvents. Now, we report on a new vicinal-dioxime ligand in which these donor groups are directly bound to N-pivot atoms of two monoaza[15]crown-5 units and on its Ni(II), Pt(IV), and Pd(II) complexes. The Pd(II) complex has been subjected to single-crystal X-ray diffraction analysis.

Results and Discussion. – *Syntheses.* The 1,2-bis[(monoaza[15]crown-5)-*N*-yl]-glyoxime(=LH$_2$) was synthesized from monoaza[15]crown-5 [17] and cyanogen di-*N*-oxide. The latter was obtained by treating a suspension of (*E*,*E*)-dichloroglyoxime in CH_2Cl_2 with 1M aq. Na_2CO_3 at −40° [15] [18] [19]. The elemental analysis of the yellowish oily LH$_2$ purified by column chromatography corresponds to $C_{22}H_{42}N_4O_{10}$. A symmetrical s-*trans* form is expected for LH$_2$.



LH$_2$

In the IR spectrum of LH$_2$, the OH, C=N, and N–O stretching vibrations are observed at 3400, 1615, and 940 cm^{-1}, respectively, in agreement with values reported for similar compounds [6] [12] [15] [19]. The ^{1}H-NMR spectrum ((D$_6$)DMSO) exhibits signals for OH (8.93 ppm) and CH$_2$ groups (3.56–3.16 ppm). When $CDCl_3$ or (D$_6$)acetone is used as solvent, the OH signal is not observed due to self-association through H-bridges [20]. In the ^{13}C-NMR spectrum ((D$_6$)DMSO), the carbohydroximamide C-atom is found at 151.25 ppm [15]. The *C*H$_2$ attached to the N-atom show lower chemical shifts (50.35 ppm) than the other *C*H$_2$ (71.08–70.11 ppm).

To prepare Ni(II), Pd(II), and Pt(IV) complexes of LH_2, a solution of the ligand and a metal salt in EtOH was heated to 70° for at least 2 h while an equivalent amount of NaOH in EtOH was added gradually in the case of Ni(II) and Pd(II) complexes (see *Exper. Part*). Thus, the perchlorate complexes $[Ni(LH)_2] \cdot 4\ NaClO_4$ and $[Pd(LH)_2] \cdot 4\ NaClO_4$ and $[PtCl_2(LH)_2] \cdot 4\ NaCl$ were obtained. The $NaClO_4$-free complexes $[Ni(LH)_2]$ and $[Pd(LH)_2]$ were formed on dissolution of the corresponding perchlorates in DMSO and crystallization at room temperature. All complexes are diamagnetic indicating a square-planar structure for Ni(II) and Pd(II) (d^8) and an octahedral structure for Pt(IV) (d^6).

All complexes have IR spectra very similar to those of LH_2, except for the disappearance of the OH stretching frequencies. Weak bands at *ca.* 1740 cm^{-1} indicate $OH \cdots O$ bridges [2] [12] [15] [16], while the C=N vibrations are at lower wavenumbers, as expected for *N,N*-chelated vicinal-dioxime complexes [3] [12] [15] [16] [21]. The $NaClO_4$ content is shown by characteristic vibrations of ClO_4^- at 1140–1080 cm^{-1} [12]. In the octahedral Pt(IV) complex, the stretching vibrations of the axially arranged Cl–Pt–Cl moiety are observed at 340 cm^{-1} [22]. $OH \cdots O$ bridges appear in the ^1H-NMR spectrum as br. *s* at *ca.* 17 ppm for Ni(II) and Pd(II) and at 13.8 ppm for Pt(IV) complexes. In the ^{13}C-NMR spectra, the CH_2 of the macrocycles are also shifted to higher field in the case of the Pt(IV) complex, while there is no significant difference for the oxime C-atoms.

X-Ray Structure of [Pd(LH)₂] (see *Table 1*). The crystallographic centre of symmetry occupied by the metal determines the exact planarity of the O(1)–N(1)–Pd–N(1')–O(1') moiety of the molecule *(Fig.)*. The Pd–N distances observed, 1.978(3) and 1.970(3) Å, are comparable to the average Pd–N distances found in other examples [5–7]. The N–C and O–C distances of the macrocyclic rings are in the expected range and show no significant aberrations. In a final *ΔF* map, there was no possibility to localize an H-atom between O(1) and O(2'), but the IR spectra *(vide supra)* and the distance of 2.57 Å between the two O-atoms indicate the postulated H-bridges $OH(1) \cdots O(2')$.

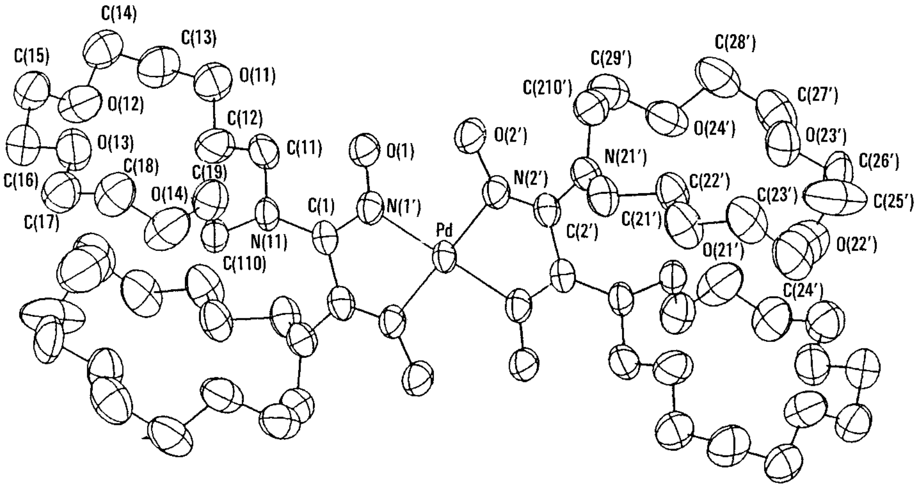


Figure. *ORTEP plot of [Pd(LH)₂]*. Arbitrary numbering.

Table 1. *Crystal Data and Data Collection Parameters for [Pd(LH)$_2$]*

Formula	$C_{46}H_{82}N_8O_{20}Pd$	Crystal size [mm]	0.2 × 0.1 × 0.1
Crystal system and space group	monoclinic, $P2_1/c$ (No. 14)	Temperature [K]	293
		Θ_{max} [°]	26
a [Å]	9.373 (1)	Radiation	MoK_α (λ = 0.71069 Å)
b [Å]	16.345 (4)	Scan type	$\omega/2\Theta$
c [Å]	17.973 (8)	No. of independent reflections	5454
α [°]	90.0		
β [°]	103.57 (2)	No. of refl. used in refinements	3716 ($F > 2\sigma(F)$)
γ [°]	90.0		
V [Å^3]	26.76.6	No. of variables	331
Z	2	Final R_w	0.0566
		Weighting system	$1/(\sigma^2(F)\ 0.00264\ F^2)$

The distances between O-atoms of a macrocycle and the corresponding O-atoms of a neighbouring macrocycle within the molecule range from 3.6–5.3 Å. This suggests the possibility of forming an intramolecular sandwich-type complex with alkali-metal ions *(vide infra)*.

The unit cell contains two centro-symmetric molecules, the two metal centres having a distance of 13.99 Å. But the orientation of the two molecules in the unit cell is such that two macrocycles have intermolecular distances which are close enough to form further interactions with alkali-metal ions; *e.g.* O(14; molecule 1)–O(12′; molecule 2) is 4.89 Å and O(14; molecule 1)–O(11′; molecule 2) is 5.95 Å.

Solvent Extraction of Alkali-Metal Cations. The alkali ion binding property of the complexes having four crown-ether units was estimated by solvent extraction of alkali-metal picrates from the aqueous to an organic phase *(Table 2)*. Since the ligand is deprotonated in basic solutions, its alkali-binding property cannot be measured under these conditions. For comparison, the values obtained under the same conditions for benzo[15]crown-5 are included in *Table 2*. Both [Ni(LH)$_2$] and [Pd(LH)$_2$] exhibit the highest affinity for K$^+$ among the alkali cations. A possible explanation is found in the spatial orientation of the crown-ether units allowing formation of sandwich-type structures for which K$^+$ should be the most suitable one.

Table 2. *Solvent Extraction of Alkali Metal* (M) *Picrates into the Organic Phase* (CH_2Cl_2) *at 25°*[a])

	Extracted picrate in %				
	Li^+	Na^+	K^+	Rb^+	Cs^+
Benzo[15]crown-5	1.40	17.8	33.6	11.3	6.2
[Ni(LH)$_2$]	12.7	10.0	40.9	22.5	4.6
[Pd(LH)$_2$]	21.1	17.8	44.5	35.1	8.6

[a]) Organic phase: [crown-ether unit] = $7 \cdot 10^{-4}$ M; aqueous phase: [MOH] = 0.1M, [picric acid] = $7 \cdot 10^{-5}$ M.

Experimental Part

General. UV/VIS: *Varian-DMS-90* spectrophotometer. IR spectra: *Perkin-Elmer-983* spectrophotometer (KBr pellets). ^{1}H- and ^{13}C-NMR spectra: *Bruker-200-MHz* spectrophotometer. Monoaza[15]crown-5 [17] and dichloroglyoxime [23] [24] were synthesized according to published procedures.

*1,2-Bis[(monoaza[15]crown-5)-*N*-yl]glyoxime (= 1,2-Bis[1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl]ethanedione Dioxime: LH_2).* Monoaza[15]crown-5 (2.3 g, 10.48 mmol) in 150 ml of CH_2Cl_2 was stirred at –40°. A soln. of cyanogen di-*N*-oxide [9] [12] in CH_2Cl_2 (125 ml) was added which was obtained by treating a suspension of dichloroglyoxime (1.2 g, 7.64 mmol) in CH_2Cl_2 with 200 ml of 1M Na_2CO_3 at –40° [9] [12] [13]. The soln. was stirred at –40° for 2 h, then allowed to warm up to r.t., dried (Na_2SO_4), and evaporated: oily residue. Column chromatography (silica gel, $CHCl_3$/MeOH 1:10) gave 1.19 g (44%) of LH_2. Yellowish oil. UV/VIS (EtOH): 314 (32), 259 (1022). IR: 3400, 2910, 2850, 1615, 1450, 1350, 1115, 940. ^{1}H-NMR ((D_6)DMSO): 8.93 (*s*, 2 NOH, disappeared by D_2O exchange); 3.56–3.34 (*m*, 32 H, CH_2O); 3.26–3.16 (*m*, 8 H, CH_2N). ^{13}C-NMR ($CDCl_3$; ^{1}H-decoupled): 151.25 (C=NOH); 71.08, 70.26, 70.11 (CH_2O); 50.35 (CH_2N). Anal. calc. for $C_{22}H_{42}N_4O_{10}$: C 50.56, H 8.10, N 10.72; found: C 49.68, H 8.32, N 10.63.

[Ni(LH)$_2$]·4 NaClO$_4$ and [Pd(LH)$_2$]·4 NaClO$_4$. To a soln. of 0.61 g (1.17 mmol) of LH_2 in 50 ml of abs. EtOH $NaClO_4 \cdot H_2O$ (0.82 g, 5.85 mmol) in 10 ml of abs. EtOH was added and heated to 70° for ½ h. The soln. was mixed with $NiCl_2 \cdot 6\,H_2O$ (0.14 g, 0.585 mmol) or Na_2PdCl_4 (prepared by stirring 0.104 g (0.585 mmol) of $PdCl_2$ and 0.068 g ((1.117 mmol) of NaCl in EtOH) in EtOH (20 ml). A decrease in pH was observed, and the mixture was stirred and heated to 75° for 2 h while an equivalent amount of NaOH was added dropwise to maintain a pH value of 5 → orange). On cooling to r.t., yellow-orange crystals precipitated. They were filtered, washed with cold EtOH and Et_2O, and dried.

Ni(LH)$_2$·4 NaClO$_4$: 0.14 g (15%). M.p. 238–240° (dec.). IR (KBr): 2900, 2860, 1740, 1620, 1550, 1440, 1350, 1140–1080, 930, 620. Anal. calc.: C 33.20, H 5.19, N 7.04; found: C 32.98, H 4.89, N 6.89.

[Pd(LH)$_2$·4 NaClO$_4$: 0.58 g (60%). M.p. 230–232° (dec.). IR (KBr): 2910, 2865, 1550, 1440, 1350, 1145–1080, 935, 620. Anal. calc.: C 32.24, H 5.04, N 6.84; found: C 32.11, H 5.09, N 6.72.

[Ni(LH)$_2$] and [Pd(LH)$_2$]. $[Ni(LH)_2] \cdot 4\,NaClO_4$ or $[Pd(LH)_2] \cdot 4\,NaClO_4$ (0.5 g) was dissolved in DMSO (7 ml) and acetone (1 ml) at 50°. On cooling to r.t., crystallization occurred.

[Ni(LH)$_2$]: Dark red crystals, 0.1 g (29%). M.p. 212–214° (dec.). UV/VIS (EtOH): 443 (3220), 388 (10360), 355 (11840), 270 (10720). IR (KBr): 2900, 2860, 1740, 1620, 1550, 1440, 1350, 1125, 930. ^{1}H-NMR (CD_3CN): 17.24 (*s*, 2 OH···O, disappeared by D_2O exchange); 3.56 (*m*, 64 H, CH_2O); 3.29 (*t*, 16 H, CH_2N). Anal. calc.: C 47.97, H 7.50, N 10.17; found: C 48.06, H 7.16, N 9.96.

[Pd(LH)$_2$]: Dark orange crystals, 0.17 g (49%). M.p. 193–195° (dec.). UV/VIS (EtOH): 340 (14760), 288 (10560). ^{1}H-NMR (CD_3CN): 18.0 (*s*, 2 OH···O, disappeared by D_2O exchange); 3.66–3.56 (*m*, 64 H, CH_2O); 3.38 (*t*, 16 H, CH_2N). ^{13}C-NMR (CD_3CN; ^{1}H-decoupled): 151.33 (C=N–O); 70.81, 70.70, 70.22, 70.13 (CH_2O); 51.78 (CH_2N). Anal. calc. for $C_{46}H_{82}N_8O_{20}Pd$: C 45.97, H 7.19, N 9.75; found: C 45.82, H 7.02, N 9.64.

[PtCl$_2$(LH)$_2$]·4 NaCl. To a soln. of LH_2 (0.496 g, 0.95 mmol) in 25 ml of EtOH was added a soln. of $Na_2PtCl_6 \cdot 6\,H_2O$ (0.281 g, 0.5 mmol) in EtOH (20 ml) and the mixture stirred and refluxed for 45 min. After cooling to r.t., the orange precipitate was filtered off, washed with EtOH and Et_2O, and dried: 0.16 g (22%). M.p. 198–200°. UV/VIS (DMSO): 277 (29950). IR (KBr): 2920, 2880, 1630, 1450, 1355, 1120–1090, 935, 340. ^{1}H-NMR ((D_6)DMSO): 13.8 (*s*, 2 OH···O); 3.75–3.52 (*m*, 64 H, CH_2O); 3.20 (*t*, 16 H, CH_2N). ^{13}C-NMR ((D_6)DMSO; ^{1}H-decoupled): 154.84 (C=N–O); 69.17, 69.09, 65.08 (CH_2O); 46.13 (CH_2N). Anal. calc.: C 34.24, H 5.35, N 7.26; found: C 34.11, H 5.28, N 7.12.

Solvent Extraction of Alkali-Metal Cations. The alkali-binding ability of $[Ni(LH)_2]$ and $[Pd(LH)_2]$ was estimated by treating aq. solns. of alkali picrates prepared from 0.1M MOH and $7 \cdot 10^{-5}$ M picric acid with solns. of the Ni(II) and Pd(II) complexes in CH_2Cl_2 ([crown-ether unit] = $7 \cdot 10^{-4}$ M). UV/VIS absorbances were measured at 355 nm before and after treatment [25] [26]. Results: *Table 2*.

X-Ray Structure of [Pd(LH)$_2$]. Crystal data and parameters of the data collection: *Table 1*. Unit-cell parameters were determined by accurate centering of 25 strong independent reflections by the least-squares method. Four standard reflections monitored every h during data collection showed no intensity loss. The raw data set was corrected for polarization effects, but no correction for absorption was applied. The structure was solved by direct methods strategies using the program SHELXS-86 [27]. Anisotropic least-squares full-matrix refinements [29] were carried out on all non-H-atoms. Positions of H-atoms are calculated. Scattering factors are from *Cromer et al.* [28] or given in the SHELX-76 program [25]. Fractional coordinates are deposited at the *Cambridge Crystallographic Data Base*. The *Figure* shows an ORTEP plot of the molecule.

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