

Metal Ion Coordinating Properties of the Highly Preorganized Tetradentate Ligand 1,10-Phenanthroline-2,9-dicarboxaldehyde-2,9-dioxime

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Use of UV/Vis spectroscopy to measure protonation and formation constants of PDOX (1,10-phenanthroline-2,9-dicarboxaldehyde-2,9-dioxime) is reported. All complexes all show a protonation constant of an oxime that is quite close to pK_{a1} for the free ligand, that is, for Zn^{II} $\log K$ for $ZnPDOX + H^+ \rightleftharpoons ZnPDOXH^+$. This is in agreement with literature crystal structures, which show that, for small metal ions such as Zn^{II} ,

one oxime group of PDOX is left non-coordinated. Only for Pb^{II} is the protonation constant of the PDOX complex significantly lowered, to a value of 8.2. In order to investigate the high $\log K_1$ value for the $Pb^{II}/PDOX$ complex, and its relatively low protonation constant, the crystal structure of $[Pb(PDOXH_2)(DMSO)_2Cl(ClO_4)]$ (**1**) was determined.

Introduction

Design and evaluation of new ligands is important^[1] in areas ranging from metal ions in medicine^[2–5] to fluorescent sensors for metal ions in biological and the environmental applications.^[6–10] An important aspect of ligand design is preorganization:^[11] preorganized ligands are those constrained to be in the conformation required to complex the target metal ion. Familiar examples of preorganized ligands are crown ethers,^[12] cryptands,^[13] and nitrogen-donor (N-donor) macrocycles.^[14] More recently, the metal ion coordinating properties of highly preorganized ligands based on the phen (see Figure 1 for key to ligand abbreviations) backbone have been reported for ligands such as PDA,^[15–17] DPP,^[18] PDALC,^[19,20] and PDAM.^[21] The rigidity of the phen backbone has led to widespread use of the phen moiety in ligand design.^[22,23]

A fundamental quantity in evaluating the complexing abilities and metal ion selectivities of ligands is the formation constant ($\log K_1$). Ligands such as PDA have shown^[22] remarkable increases in $\log K_1$ relative to less preorganized analogues such as EDDA. In addition, ligands such as PDA, DPP, PDALC, and PDAM display strong size-based selectivity for metal ions that depends on the presence of not a cavity but a rigid cleft.^[22] Metal ion complexation rates with ligands possessing rigid clefts are rapid,^[22] unlike other preorganized ligands such as macrocycles. This can be a distinct advantage in applications such as the development of solvent extractants for selective recovery of metal

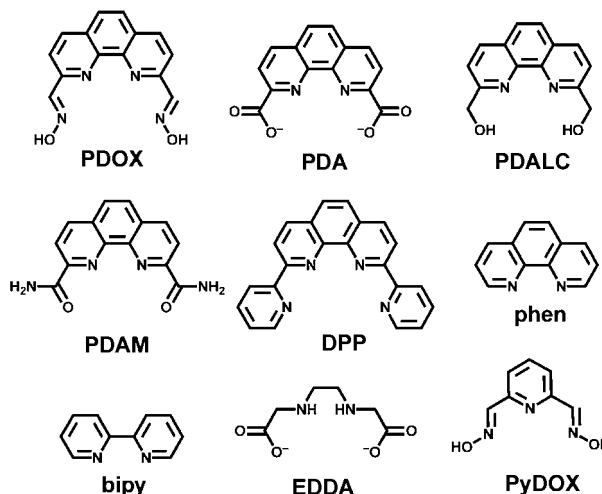


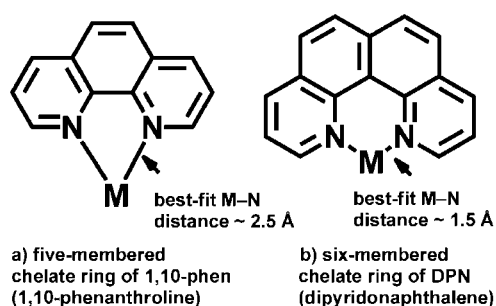
Figure 1. Ligands discussed in this paper.

ions such as the separation of Am^{III} from Ln^{III} (Ln = lanthanide) in the treatment of nuclear waste.^[24] Am^{III} differs from Ln^{III} ions in its chemistry largely only in forming slightly more covalent $M-L$ (L = ligand) bonds.^[25,26] This has led to the investigation of a variety of N-donor ligands with donor atoms of the pyridyl type as the potential basis for separation of the more covalently bound Am^{III} from Ln^{III} ions.^[27–36] The available evidence^[27–36] suggests that the more N donors a ligand has, the greater the advantage for selective complexation of Am^{III} . Following this line of logic, the ligand PDOX (Figure 1) has been investigated because of its four sp^2 hybridized N donors, which might lead to enhanced selectivity for Am^{III} relative to ligands with fewer N donors. Some work has already been reported on PDOX, such as on its synthesis,^[37] and on the structures of its com-

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plexes with Cu^{II} , Ni^{II} , Zn^{II} , Cd^{II} , and Co^{II} .^[38] These studies showed that small^[39] metal ions such as Cu^{II} , Ni^{II} , Zn^{II} , and Co^{II} are unable to coordinate simultaneously to all four N donors of PDOX, paralleling structures of, for example, Ni^{II} with PDA,^[40] where one carboxylate group is left uncoordinated to the Ni^{II} . Two structures for the larger^[39] Cd^{II} ion were reported,^[38] one of which had a PDOX coordinated to the Cd^{II} through only three N donors, while the other was nominally tetradentate, although with very long Cd–N bonds involving the oxime N donors. A large amount of evidence^[1] suggests that ligands that form exclusively five-membered chelate rings will show selectivity for large metal ions with ionic radii in the vicinity of 1.0 Å, whereas alteration of the ligand to produce analogues that form six-membered chelate rings shifts selectivity in the direction of smaller metal ions as more six-membered chelate rings are present. This size-based selectivity can be understood in terms of Scheme 1.



Scheme 1. Best-fit M–N lengths for metal ions coordinating with an aromatic heterocyclic N-donor ligand that forms (a) a five membered chelate ring, or (b) a six-membered chelate ring.

PDOX is a ligand that forms exclusively five-membered chelate rings, and as such should be well-suited for complexation of large metal ions such as Am^{III} [ionic radius^[39] (r^+) = 0.98 Å (octahedral coordination)]. Since PDOX should be well-suited for the complexation of large metal ions, the structure of the complex of PDOX with Pb^{II} [ionic radius^[39] (r^+) = 1.19 Å] is reported here. In order to evaluate the metal ion complexing abilities of PDOX in aqueous solution, its protonation constants and formation constants with Ca^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} , La^{III} , and Pb^{II} , all in aqueous solution, are reported here.

Results and Discussion

Formation Constants

The protonation constants reported here for PDOX of $\text{p}K_{\text{a}1}$ = 10.55(5), $\text{p}K_{\text{a}2}$ = 9.95(5), and $\text{p}K_{\text{a}3}$ = 3.26(3) (Table 1) in 0.1 M NaClO_4 at 25 °C are much as would be expected by comparison with the analogous PyDOX (Figure 1), which has a pyridine in place of the phen of PDOX, where^[42] $\text{p}K_{\text{a}1}$ = 10.54, $\text{p}K_{\text{a}2}$ = 9.91, and $\text{p}K_{\text{a}3}$ = 2.18. The oxime groups appear to lower the $\text{p}K_{\text{a}}$ values of the pyridine nitrogen in PyDOX relative to those in pyridine itself ($\text{p}K_{\text{a}}$ = 5.24),^[42] but do so less in PDOX because each pyridyl

group has a single oxime attached to it. A marked feature of the formation constants for PDOX reported in Tables 1 and 2 is how little the protonation constants of the oxime groups are generally lowered by coordination to a metal ion relative to those of the free ligand. Thus, $\text{p}K_{\text{a}1}$ for free PDOX is 10.55, but on coordination even to quite a large metal ion such as Cd^{2+} (r^+ = 0.96 Å), the $\text{p}K_{\text{a}1}$ for the complex is still quite high at 9.1, and, for a small metal ion such as Zn^{2+} (r^+ = 0.74 Å), the $\text{p}K_{\text{a}1}$ is 10.6, essentially the same as that for the free ligand. Interestingly, the structures^[38] of the PDOX complexes of Cu^{II} , Ni^{II} , Zn^{II} , and one of the two Cd^{II} structures with PDOX have the diprotonated form of PDOX coordinated to the metal ion, and in each case one of the two protonated oxime groups is not coordinated to the metal ion at all, and is in fact in the *exo* form (Scheme 2).

Table 1. Protonation and formation constants for PDOX measured here (25 °C, 0.1 M NaClO_4).

Lewis acid	Equilibrium	$\log K$	Reference
H^+	$\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$	13.78	[42]
	$\text{H}^+ + \text{PDOX}^{2-} \rightleftharpoons \text{PDOXH}^-$	10.55(5)	this work
	$\text{H}^+ + \text{PDOXH}^- \rightleftharpoons \text{PDOXH}_2$	9.95(5)	this work
	$\text{H}^+ + \text{PDOXH}_2 \rightleftharpoons \text{PDOXH}_3^+$	3.26(3)	this work
Zn^{2+}	$\text{Zn}^{2+} + \text{PDOX}^{2-} \rightleftharpoons \text{ZnPDOX}$	8.9(1)	this work
	$\text{ZnPDOX} + \text{H}^+ \rightleftharpoons \text{ZnPDOXH}^+$	10.6(1)	this work
Cd^{2+}	$\text{Cd}^{2+} + \text{PDOX}^{2-} \rightleftharpoons \text{CdPDOX}$	9.7(1)	this work
	$\text{CdPDOX} + \text{H}^+ \rightleftharpoons \text{CdPDOXH}^+$	9.1(1)	this work
Pb^{2+}	$\text{Pb}^{2+} + \text{PDOX}^{2-} \rightleftharpoons \text{PbPDOX}$	11.4(1)	this work
	$\text{PbPDOX} + \text{H}^+ \rightleftharpoons \text{PbPDOXH}^+$	8.2(1)	this work
Ca^{2+}	$\text{Ca}^{2+} + \text{PDOX}^{2-} \rightleftharpoons \text{CaPDOX}$	5.4(1)	this work
	$\text{CaPDOX} + \text{H}^+ \rightleftharpoons \text{CaPDOXH}^+$	10.6(1)	this work
La^{3+}	$\text{La}^{3+} + \text{PDOX}^{2-} \rightleftharpoons \text{LaPDOX}^+$	8.5(1)	this work
	$\text{LaPDOX}^+ + \text{H}^+ \rightleftharpoons \text{LaPDOXH}^{2+}$	10.04(3)	this work
Gd^{3+}	$\text{Gd}^{3+} + \text{PDOX}^{2-} \rightleftharpoons \text{GdPDOX}^+$	8.8(1)	this work
	$\text{GdPDOX}^+ + \text{H}^+ \rightleftharpoons \text{GdPDOXH}^{2+}$	9.96(1)	this work
UO_2^{2+}	$\text{UO}_2^{2+} + \text{PDOX}^{2-} \rightleftharpoons \text{UO}_2\text{PDOX}$	9.3(1)	this work
	$\text{UO}_2\text{PDOX} + \text{H}^+ \rightleftharpoons \text{UO}_2\text{PDOXH}^+$	10.04(3)	this work
Cu^{2+}	$\text{Cu}^{2+} + \text{PDOX}^{2-} \rightleftharpoons \text{CuPDOX}$	13.5(1)	this work
	$\text{Cu}^{2+} + \text{PDOXH}_2 \rightleftharpoons \text{CuPDOXH}_2^{2+}$	7.2(1)	this work

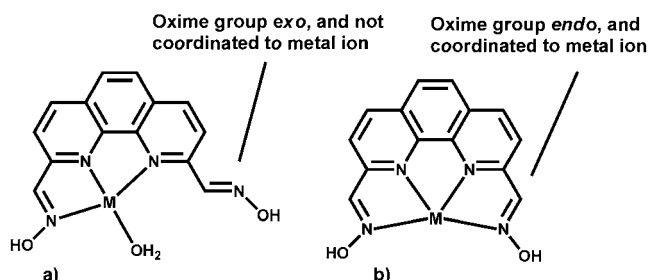
Table 2. Comparison of formation constants of PDOX and phen with a variety of Lewis acids.

Lewis acid	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ca^{2+}	La^{3+}	Gd^{3+}	Pb^{2+}	H^+
Ionic radius ^[a]	0.57	0.74	0.96	1.00	1.03	0.94	1.19	
$\log K_1(\text{PDOX})$	13.5	8.9	9.7	5.4	8.5	8.8	11.4	
$\log K_1(\text{phen})$ ^[c]	9.1	6.4	5.7	1.0	1.85 ^[d]	2.3 ^[d]	4.6	
$\Delta \log K$ ^[e]	4.4	2.5	4.0	4.4	6.7	6.5	6.8	
$\text{p}K_{\text{a}1}$ ^[f]	9.87	10.6	9.1	10.6	10.04	9.96	8.2	10.55

[a] Units are Å, octahedral radii, except Cu^{II} (square planar) ref.^[39]

[b] Ionic strength 0.1, this work. [c] Ionic strength 0.1, ref.^[42] [d] Ref.^[54] [e] Change in $\log K_1$ in passing from the phen to the PDOX complex, i.e. $\log K_1(\text{PDOX}) - \log K_1(\text{phen})$. [f] The protonation constant of the complex, i.e. $\log K$ for $\text{ML} + \text{H}^+ \rightleftharpoons \text{MLH}^+$, except for H^+ which is $\log K$ for $\text{L} + \text{H}^+ \rightleftharpoons \text{LH}^+$ ($\text{L} = \text{PDOX}$).

Table 2 shows that PDOX stabilizes complexes with large metal ions such as La^{III} and Pb^{II} quite considerably relative to phen. For a small metal ion such as Zn^{II} , the stabilization



Scheme 2. Coordinated PDOX ligands with (a) one oxime group *exo* and not coordinated to the metal ion (M), and (b) the coordinated oxime groups both *endo*.

of the PDOX relative to the phen complex is quite small. The high basicity of the coordinated oxime groups in the PDOX complexes is perhaps not surprising in that the oxime groups coordinate to metal ions through the nitrogen atom, while the proton attaches to the oxygen atom, although one might have expected some of the negative charge on the deprotonated form of the oxime group to be delocalized onto the nitrogen atom. A reviewer has commented on the high stability of the Cu^{II} complex of PDOX, in spite of the fact that Cu^{II} is a small^[39] metal ion. This high stability of the PDOX complex of Cu^{II} arises from the fact that Cu^{II} is a strong Lewis acid with N-donor ligands, as can be ascertained from the $\log K_1(\text{phen})$ values in Table 2, so that Cu^{II} is stabilized quite considerably by coordination to the N-donor atom of even a single oxime group. The stabilization of the Cu^{II} complex of PDOX relative to the phen complex is still small relative to large metal ions such as La^{III} or Pb^{II} , which fit PDOX sterically much better than does Cu^{II} , in spite of the much lower affinity of the latter ions for N donors. A further query has been whether $\Delta \log K_1$ in Table 2 varies linearly with ionic radius of the metal ion. The answer is that it does not, since the increase in $\log K_1$ for the PDOX relative to the phen complex of each metal ion depends not only on metal ion size, but also on the affinity of the metal ion for the N donors of the oxime group, as discussed for Cu^{II} above. Of particular interest in Table 2 is the very large stabilization of the PDOX complex of Pb^{II} relative to its phen complex, which may relate to the ability of such a large metal ion ($r^+ = 1.19 \text{ \AA}$ for Pb^{II}) to coordinate with both of the oxime groups of PDOX in the *endo* form.

The Structure of $[\text{Pb}(\text{PDOXH}_2)(\text{DMSO})_2\text{Cl}(\text{ClO}_4)]$ (1)

The complex of PDOX with Pb^{II} is shown in Figure 2, and bond lengths and angles of interest are given in Table 3. The structure shows that the Pb^{II} in **1** has both oxime groups protonated, but unlike previously reported structures of PDOX, except for one of two Cd^{II} structures,^[38] both oxime groups are in the *endo* form and are coordinated to the Pb with Pb–N bond lengths of 2.625(6) and 2.909(6) \AA . The two pyridyl nitrogen atoms of PDOX are coordinated to the Pb^{II} with relatively short Pb–N bond lengths of 2.544(6) and 2.631(6) \AA . Other atoms within pos-

sible bonding distance of the Pb^{II} are a coordinated chloride [$\text{Pb}–\text{Cl}$ 2.684(2) \AA], a DMSO coordinated through an oxygen atom [$\text{Pb}–\text{O}(12)$ 2.617(7) \AA], and a perchlorate [$\text{Pb}–\text{O}(7)$ 3.035(7) \AA]. A further perchlorate has the $\text{Pb}–\text{O}(6)$ distance of 3.817(7) \AA , which might be considered to be too long to be a Pb–O bond. The coordination geometry of the Pb atom in **1** is typical of that of Pb^{II} with a stereochemically active lone pair of electrons.^[43–46] What one finds is that the Pb–L (L = ligand) bond lengths are shortest on the side of the Pb away from the proposed site of the lone pair of electrons. In the case of **1**, the shortest bond, allowing for differences in the covalent radii^[47] of the donor atoms, is the Pb–Cl bond, bearing in mind that the covalent radius of Cl is^[47] 0.31 \AA larger than that for N. Other short bonds close to the Pb–Cl bond are the two pyridyl N donors of PDOX, and one of the N donors of a coordinated oxime group. As one moves away from the coordinated Cl, the Pb–L bonds become progressively longer, until one reaches the perchlorate, where a long Pb–O contact [$\text{Pb}–\text{O}(6)$] of 3.817(7) \AA is found, which is presumably close to the site of the lone pair. Excluding the latter rather long Pb–L contact, the Pb^{II} may be viewed as being 7-coordinate. A reviewer has quite reasonably queried whether one can regard the Pb–O(6) contact as a bond. The O(6) atom in contact with the Pb atom is part of a perchlorate which is held in place, as shown in Figure 2, by a hydrogen bond to the O(2) hydroxy group of a coordinated oxime. Although long Pb–O contacts in the range 3.5–4.0 \AA from anions such as ClO_4^- or NO_3^- , which are situated near the proposed site of the lone pair, are common,^[48] it is not clear whether these in any way contribute to Pb–L bonding.

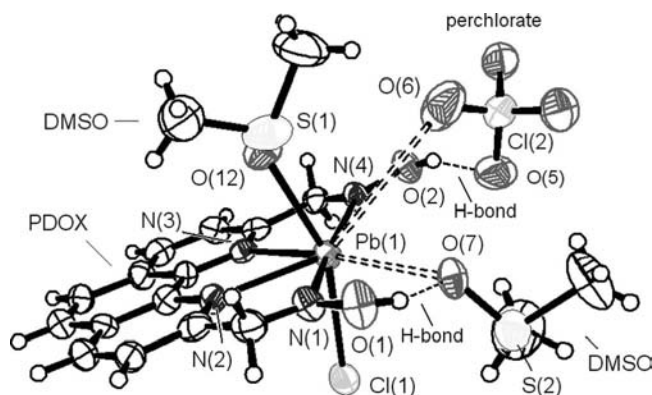


Figure 2. Structure of the Pb^{II} complex with PDOX from **1**, showing the numbering scheme for donor atoms coordinated to the Pb atom. The Pb^{II} has geometry typical of the presence of a stereochemically active lone pair of electrons, with short bonds to the N donors of PDOX, coordinated on the side away from the lone pair, a long bond to the DMSO bonding through O(7) (3.035 \AA), and a long contact with O(6) of the ClO_4^- (3.817 \AA) and on the side of the Pb^{II} where the lone pair is proposed to occur. The sulfur atoms of both DMSO molecules were disordered, and only one position of each is shown. The drawing, made with ORTEP,^[41] shows thermal ellipsoids at the 50% confidence level.

Some 40 structures of complexes of PyDOX and related pyridine-based dioxime ligands have been reported.^[48] All of these show that, even with small metal ions such as Cu^{II}

Table 3. Selected bond angles and lengths for [Pb(PDOXH₂)-(DMSO)Cl(ClO₄)₂] (1).

Bond lengths [Å]			
Cl(1)–Pb(1)	2.684(2)	Pb(1)–N(2)	2.544(6)
Pb(1)–O(12)	2.617(7)	Pb(1)–N(1)	2.625(6)
Pb(1)–N(3)	2.631(6)	Pb(1)–N(4)	2.909(6)
Pb(1)–O(7)	3.035(7)	Pb(1)–O(6)	3.817(7)
Bond angles [°]			
N(2)–Pb(1)–O(12)	75.3(2)	N(2)–Pb(1)–N(1)	62.4(2)
O(12)–Pb(1)–N(1)	82.1(2)	N(2)–Pb(1)–N(3)	63.95(19)
O(12)–Pb(1)–N(3)	85.5(2)	N(1)–Pb(1)–N(3)	126.31(19)
N(2)–Pb(1)–C(11)	80.43(15)	O(12)–Pb(1)–Cl(1)	155.50(15)
N(1)–Pb(1)–Cl(1)	84.00(16)	N(3)–Pb(1)–Cl(1)	86.66(14)

or Zn^{II}, both oxime groups are coordinated to the metal ion. One can thus conclude that it is preorganization for coordination of large metal ions by PDOX, provided by the phen backbone of the ligand, that leads to non-coordination of an oxime group with all metal ions so far studied,^[38] except for a Cd^{II} ($r^+ = 0.96$ Å) structure, and the very large Pb^{II} ion ($r^+ = 1.19$ Å) reported here. The Pb–N bonds to the N donors of the oximes of PDOX, and the Cd–N bonds of the PDOX complex in which PDOX appears to act as a tetradentate ligand^[38] with Cd^{II} are rather long. The Pb–N bonds to the oxime N donors average 2.767 Å, relative to the Pb–N bonds to the pyridyl N donors of PDOX, which average 2.588 Å. For the Cd^{II} complex, the difference is even more marked, Cd–N bonds to the oxime N donors averaging 2.750 Å and to the pyridyl N donors averaging 2.355 Å.^[38] It appears that the best-fit M–N length to the oxime N donors of PDOX might be very long. This can be supported by the structure of the free ligand,^[38] which contains one PDOX molecule with the *exo-exo* conformation and one *exo-endo* form. One can take the *exo-endo* form and use a model-building program such as HyperChem^[49] to rotate the *exo* oxime group into the *endo* position. This suggests an N···N distance between the two oxime N donors of 5.35 Å, which would correspond to a best-fit M–N length of about 2.68 Å. In line with the oxime M–N distances averaging 2.767 Å for Pb^{II}, and 2.750 Å for Cd^{II}, this suggests that the latter long M–N distances are largely controlled by the geometry of the ligand. This requirement of long M–N distances to the oxime N donors of PDOX accounts for its tendency to act only as a tridentate ligand with smaller metal ions. This tendency to act only as a tridentate ligand has led to examples in which the *exo* oxime group of PDOX can bridge with neighboring metal ions. Thus, trinuclear and hexanuclear clusters of PDOX complexes of the small Co^{III} and Fe^{III} ions, in which one *exo* oxime group from each coordinated PDOX bridges a neighboring metal ion have recently been reported.^[50,51]

Conclusions

PDOX forms complexes of considerable stability, particularly with larger metal ions such as La^{III}, Gd^{III}, and Pb^{II}. The rigid phen backbone of PDOX leads to high levels

of preorganization, which favors larger metal ions because^[1] of the exclusive formation of five-membered chelate rings by PDOX. The effect of this high level of preorganization is that the large Pb^{II} ion forms a complex with PDOX where both oxime groups are coordinated to the metal ion, in contrast to the PDOX complexes of smaller metal ions, where^[38] one oxime group is left non-coordinated. In spite of the fairly strong complexation of metal ions of interest such as La^{III} and Gd^{III} by PDOX, the decomposition of the ligand over a period of days in solution at low pH suggests that PDOX might be problematic as the functional group of solvent extractants^[24] for the separation of, for example, Am^{III} from the Ln^{III} ions.

Experimental Section

Materials and Methods: PDOX was synthesized by a literature method.^[37] The metal perchlorates were obtained from VWR or Strem in 99% purity or better and used as received. All solutions were made up in deionized water (Milli-Q, Waters Corp.) of > 18 MΩcm^{−1} resistivity.

[Pb(PDOXH₂)(DMSO)₂Cl(ClO₄)₂] (1): The synthesis followed the methods used^[38] for other M^{II} complexes of PDOX. To a solution of PDOX (10 mL) in DMSO was added one equivalent of Pb(ClO₄)₂·3H₂O (Alfa Aesar) dissolved in ethanol (10 mL). After heating at reflux for one hour to ensure complete solution of the PDOX, and storage for a few days, colorless crystals of **1** precipitated out. C₁₈H₂₂Cl₂N₄O₈PbS₂ (764.62); calcd. C 28.27, H 2.90, N 7.33; found C 28.12, H 2.99, N 7.05.

Molecular Structure Determination: A Rigaku Mercury diffractometer with the omega scan mode was employed for crystal screening, unit cell determination, and data collection. The structure was solved by direct methods and refined to convergence.^[52] Both the DMSO molecules were disordered in a manner similar to that found^[38] for previously reported structures of PDOX complexes containing DMSO molecules. In each case, more than one partial sulfur atom was refined. In the case of the solvate, the two minor sulfur components were refined isotropically, because their anisotropic parameters became negative. Some details of the structure determination are given in Table 4, and crystal coordinates and details of the structure determination of **1** have been deposited with

Table 4. Details of structure determination of [Pb(PDOXH₂)-(DMSO)₂Cl(ClO₄)₂] (1).

Empirical formula	C ₁₈ H ₂₂ Cl ₂ N ₄ O ₈ PbS ₂
Formula weight	764.62
Temperature [K]	158(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	
<i>a</i> [Å]	15.5877(16)
<i>b</i> [Å]	11.5694(16)
<i>c</i> [Å]	14.7589(19)
β [°]	103.559(6)
Volume [Å ³]	2587.4(6)
<i>Z</i>	4
Goodness of fit on <i>F</i> ²	1.043
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0441, <i>wR</i> 2 = 0.0585
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1060, <i>wR</i> 2 = 0.1197

the CSD (Cambridge Structural Database).^[48] Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-810242 (for 1). A selection of bond lengths and angles for 1 is given in Table 3. The structure of 1 is shown in Figure 2.

Formation Constant Determination: Formation constants were determined by UV/Vis spectroscopy by following procedures similar to those reported previously^[15–20] for studying complexes of PDA, PDALC, or DPP. UV/Vis spectra were recorded with a Varian 300 Cary 1E UV/Vis Spectrophotometer controlled by Cary Win UV Scan Application version 02.00(5) software. A VWR symphony™ SR60IC pH meter with a VWR symphony™ gel epoxy semimicro combination pH electrode was used for all pH readings, which were made in the external titration cell, with N₂ bubbled through the cell to exclude CO₂. The pH meter was calibrated prior to each titration, by means of the titration of standard acid with standard base: the value of E° for the cell, as well as the Nernstian slope, was obtained from a linear plot of measured values of E vs. the calculated pH. The cell containing ligand/metal solution (50 mL) was placed in a bath thermostatted to 25.0 ± 0.1 °C, and a peristaltic pump was used to circulate the solution through a 1.0 cm quartz flow cell situated in the spectrophotometer. The pH was altered in the range 2 to 12 by additions to the external titration cell of small amounts of standard HClO₄ or NaOH as required with a micropipette. After each adjustment of pH, the system was allowed to mix by operation of the peristaltic pump for 15 min prior to recording the spectrum, and to ensure proper mixing, the solution in the external cell was agitated with a magnetic stirrer.

PDOX is not very water soluble (ca. 10^{-4} M), but has intense bands in the UV that can be used to monitor complex formation in solution. A problem with PDOX that became apparent was that 10^{-4} M solutions of PDOX that were used as stock solutions decomposed at pH 2.0 over the course of a few days, as evidenced by progressive changes in the electronic spectra. As a result, solutions of PDOX were made up and used the same day to avoid problems with decomposition. The spectra of PDOX solutions (10^{-5} M) at different pH values in NaClO₄ (0.1 M) at 25 °C are shown in Figure 3. The variations in absorbance as a function of pH at five different wavelengths for the PDOX solutions in Figure 3 are given in Figure 4. The solid lines in Figure 4 are theoretical curves of absorbance vs. pH fitted to the experimental data points by using the SOLVER

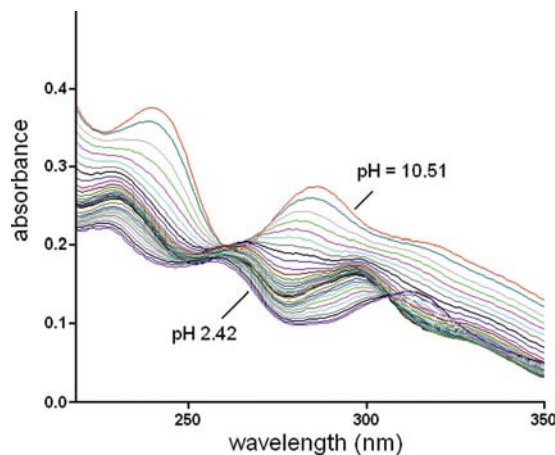


Figure 3. Spectra of 10^{-5} M PDOX at 25 °C in 0.1 M NaClO₄ at a pH range of 2.42 to 10.51.

module of EXCEL.^[53] For a set of spectra for any one metal ion with PDALC, SOLVER^[53] was used to fit protonation constants and molar absorptivities for the species in solution involving PDALC. The spectra of Zn^{II} (10^{-5} M) with PDOX (10^{-5} M) at a pH range of 2.49 to 10.59 are shown in Figure 5. The standard deviations given in Table 1 were calculated by using the SOLVSTAT macro provided with ref.^[53]

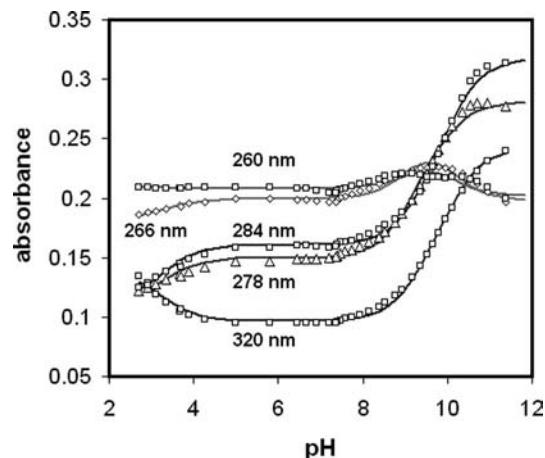


Figure 4. Variation of absorbance as a function of pH for 10^{-5} M PDOX at 25 °C in 0.1 M NaClO₄ at five different wavelengths. Points are the experimental values, solid lines are theoretical curves generated from the three pK_a values for PDOX given in Table 1, fitted with EXCEL.^[53]

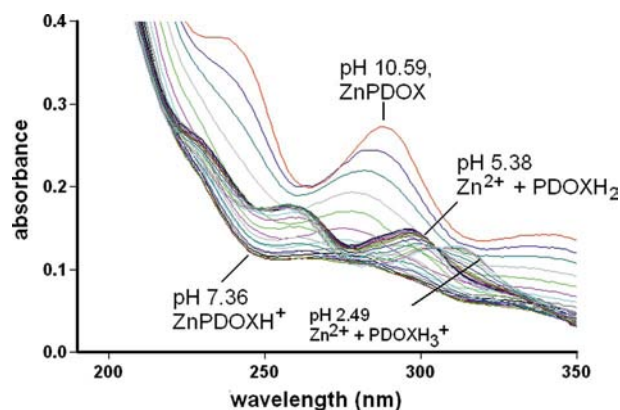


Figure 5. Spectra of 10^{-5} M PDOX and 10^{-5} M Zn²⁺ at 25 °C in 0.1 M NaClO₄ at a pH range of 2.49 to 10.59. As indicated on the diagram, at pH 10.59 the species present is ZnPDOX, at pH 7.36 it is ZnPDOXH⁺, and at pH 5.38 this has broken up to yield Zn²⁺ and the deprotonated PDOXH₂. Further protonation occurs to give PDOXH₃⁺, the isosbestic point at 305 nm confirming that the PDOX species in solution are PDOXH₂ and PDOXH₃⁺.

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