METAL-ORGANIC COMPOUNDS

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Aqua[9-(1,8-diazafluoren-9-ylidene)amino-1,8-diazafluorenato]hydroxo(urea)zinc(II) urea solvate

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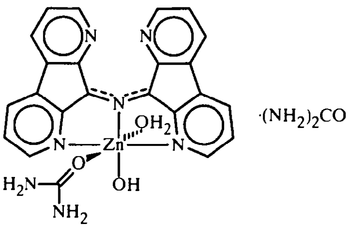
Abstract

1,8-Diazafluoren-9-one (DFO) reacts with amino acids to produce a red fluorescent pigment whose fluorescence is enhanced by zinc ions. We report here the structure of the purple zinc complex, $[Zn(C_{22}H_{12}N_5)(OH)(CH_4N_2O)(H_2O)]\cdot CH_4N_2O$, formed by this pigment. The ligand binds to zinc *via* three N atoms, and the other coordination sites in the distorted octahedron are occupied by H_2O, OH^- and urea. The structure bears many similarities to analogous compounds prepared from ninhydrin.

Comment

The reagent 1,8-diazafluoren-9-one (DFO) is used in forensic investigations to detect latent fingerprints (Pounds *et al.*, 1990). DFO reacts with amino acids on paper and similar materials to produce a red pigment which fluoresces around 580–620 nm, depending on the exact conditions used. Treatment of this pigment on filter paper with a solution containing zinc salts leads to a slight increase in fluorescence (Canta *et al.*, 1993). The structure of the pigment has been inferred from solution NMR data and by analogy with related ninhydrin systems to be a symmetrical azomethine ylide or a protonated or deprotonated form thereof (Grigg *et al.*, 1989, 1990). Such a structure would have a tridentate binding site suitable for complexing to metal ions.

We have now confirmed that this structure, (I), occurs in the species formed when the pigment reacts with Zn^{II} ions. The structure (Fig. 1) shows that the aza bridge is symmetric, rather than having localized double and single C—N bonds. The Zn^{II} ion is six-coordinate and is bonded to three of the N atoms in the ligand, with the remaining zinc coordination sites being occupied by water, hydroxide and urea. Significant bond distances and angles are given in Table 1. The central C—N—C angle [137.4 (4)°] is slightly larger than the angle observed in the analog derived from ninhydrin (Ruhemann's Purple, RP) {134.5, 127.9 and 133.0° for $Na[ZnCl_2RP][ZnCl(MeOH)RP]$, protonated RP and $[Cd(RP)I(H_2O)_2]$, respectively; Davies, Taylor *et al.*, 1995; Grigg *et al.*, 1989, Lennard *et al.*, 1987}.



(I)

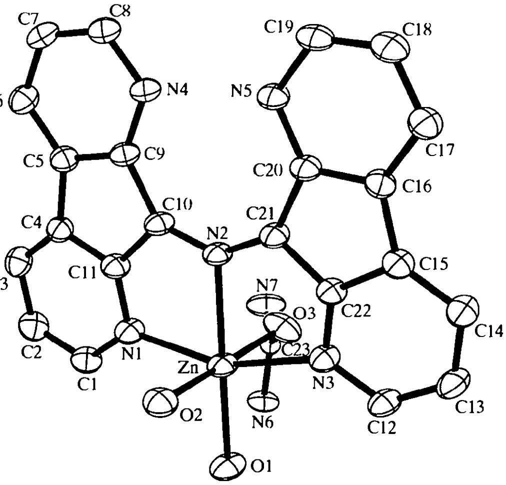


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Studies of the Ruhemann's Purple derivatives have suggested that the fluorescence of such complexes is enhanced by a decrease in the dihedral angle between the two aromatic moieties. The dihedral angle observed here (5.1°) is similar to that observed in the non-fluorescent $Na[Zn(RP)Cl_2][Zn(RP)Cl(MeOH)]$ (6.5°; Davies, Taylor *et al.*, 1995), but is smaller than that seen in the fluorescent $[Cd(RP)I(H_2O)_2]\cdot THF$ (19.5°; Lennard *et al.*, 1987), supporting the suggestion that other factors such as rigidity and ligand overlap also control the fluorescence (Davies, Kobus *et al.*, 1995). The similar dihedral angles for the two zinc complexes suggest that the Zn^{II} ion is acting to keep the two halves of the ligands approximately coplanar. The rigid nature of each half of the ligand derived from DFO mean that any steric hindrance between the two halves can only be relieved by bending or twisting of the central CNC fragment.

The Zn—O_{urea} bond [2.226 (4) Å] is significantly longer than that seen in $[Zn(H_2NCONH_2)_2(CH_3CO_2)_2]$

(1.997 and 1.994 Å; Yar & Lessinger, 1995) or $[Zn(H_2NCONH_2)_6]^{2+}$ (2.147, 2.073 and 2.019 Å; van de Giesen & Stam, 1972), while the C—O—Zn angle of 125.0 (3)° is comparable to that seen in these two complexes, *i.e.* 128.0 and 130.0° in $[Zn(H_2NCONH_2)_2(CH_3CO_2)_2]$, and 129.7, 132.2 and 132.8° in $[Zn(H_2NCONH_2)_6]^{2+}$.

The source of the urea is still under investigation, although the bond distances in the urea molecules and the extensive hydrogen-bonding network (Table 2) in the crystal structure clearly show that urea is present. In conclusion, the structure shows that the reaction of DFO with amino acids is similar to that of ninhydrin, and leads to an analogous product.

Experimental

DFO (0.515 g, 0.28 mmol) and glycine (0.123 g, 1.6 mmol) were dissolved in ethanol (20 ml) and acetic acid (10 ml) and were heated to 343–348 K with constant stirring for 1 h. The dark-red solution was allowed to cool to room temperature, and then solid NH_4PF_6 (0.25 g, 1.5 mmol) was added with stirring to give a dark red–brown precipitate. The suspension was cooled in an ice bath for 15 min, then the precipitate was filtered and washed with ice-water. The crude product (0.336 g) was dissolved in acetonitrile (80 ml) and water (30 ml), and the solution was left to evaporate. The fine needles obtained were washed with 2-propanol and diethyl ether and dried under vacuum. A small amount of this crystallized product (*ca* 10 mg) was added to acetone (10 ml) and acetonitrile (10 ml). $ZnCl_2\cdot 4H_2O$ (*ca* 2 mg) was added and the solution was sonicated and then filtered into a clean dry flask. The solution was left to evaporate and after one week, crystals suitable for X-ray crystallographic analysis had formed.

Crystal data

$[Zn(C_{22}H_{12}N_5)(OH)(CH_4N_2O)(H_2O)]\cdot CH_4N_2O$
$M_r = 566.88$
Monoclinic
$P2_1/c$
$a = 7.8637\ (3)$ Å
$b = 16.0133\ (5)$ Å
$c = 17.9513\ (6)$ Å
$\beta = 101.358\ (1)°$
$V = 2216.23\ (13)$ Å^3
$Z = 4$
$D_x = 1.687$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 7979 reflections
$\theta = 2\text{–}25°$
$\mu = 1.165$ mm^{-1}
$T = 203\ (2)$ K
Prism
0.19 × 0.19 × 0.16 mm
Purple

Data collection

Siemens SMART diffractometer
Area-detector ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.809$, $T_{max} = 0.836$

3162 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 25°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 21$

13 135 measured reflections
3895 independent reflections

Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.168$
$S = 1.054$
3895 reflections
349 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0943P)^2 + 5.2895P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.046$
$\Delta\rho_{max} = 1.196$ e Å^{-3}
$\Delta\rho_{min} = -0.925$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Zn—O1	2.043 (3)	Zn—O3	2.226 (4)
Zn—N3	2.140 (4)	O3—C23	1.266 (5)
Zn—O2	2.148 (4)	N2—C21	1.320 (6)
Zn—N1	2.158 (4)	N2—C10	1.325 (6)
Zn—N2	2.205 (4)		
C23—O3—Zn	125.0 (3)	C21—N2—C10	137.4 (4)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O4	0.83	2.09	2.885 (5)	159
O1—H1A···N6	0.83	2.52	2.942 (5)	113
O2—H2A···N8^{i}	0.84 (2)	2.05 (4)	2.736 (6)	139 (5)
O2—H2B···N6^{ii}	0.83 (2)	2.13 (3)	2.900 (5)	155 (5)
N6—H6C···O1	0.87	2.20	2.942 (5)	144
N6—H6B···O2^{iii}	0.87	2.22	2.900 (5)	135
N8—H8B···O2^{i}	0.87	2.01	2.736 (6)	141
N9—H9A···O1^{i}	0.87	1.92	2.731 (6)	155

Symmetry codes: (i) $1 - x, -y, 2 - z$; (ii) $x - 1, y, z$; (iii) $1 + x, y, z$.

The H atoms of the coordinated water molecule were located from difference maps and allowed to refine. The H atoms of the NH_2 groups were also located from difference maps, but free refinement proved unstable so these atoms were fixed geometrically. The remaining H atoms were placed geometrically and refined with a riding model. All H-atom displacement parameters were constrained to be $1.2U_{eq}$ of the carrier atom. The final electron-density difference map contains peaks of approximately ±1 e Å^{-3}, all of which are located within 1 Å of the Zn atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1244). Services for accessing these data are described at the back of the journal.

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Tetrachlorobis(hexamethylphosphoramide-*O*)digallium(II)(*Ga*—*Ga*)

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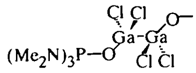
Abstract

The title compound, [$Ga_2Cl_4\{OP(C_2H_6N)_3\}$], which lies about an inversion centre, has a Ga—Ga bond length of 2.392 (1) Å and a tetrahedral arrangement about each Ga atom. The ligands adopt a staggered conformation about the Ga—Ga bond. The Raman spectrum has a band at 254 cm^{-1} assigned to the Ga—Ga stretching mode.

Comment

While simple dihalides of gallium are mixed valence compounds, other compounds show an intense band in the Raman spectrum attributable to a Ga—Ga bond (Evans & Taylor, 1969). A number of complexes of the type $Ga_2Cl_4\cdot 2L$ have been reported, along with the ionic species $Ga_2Cl_6^{2-}$ (Brown & Hall, 1973), which is constrained by space-group symmetry to have D_{3d} symmetry. The $Ga_2Cl_4\cdot 2L$ species have no such constraint and are known both with the staggered conformation, $Ga_2Cl_4\cdot$2(pyridine) (Beamish *et al.*, 1985), and in an almost eclipsed conformation, $Ga_2Cl_4\cdot$2(dioxane) (Beamish *et al.*, 1979). We now report the structure of $Ga_2Cl_4\cdot$2(hmpa), (I), for comparison with other known species (hmpa is hexamethylphosphoramide).



(I)

In $Ga_2Cl_4\cdot$2(hmpa), the Ga—Ga bond lies on an inversion centre so that the staggered conformation is adopted, as in the pyridine complex, the trimethylamine complex (Pashkov *et al.*, 1996) and Ga_2Cl_4(4-mepy)$_2$ (4-mepy is 4-methylpyridine; Gordon *et al.*, 1997), which also have a crystallographically required staggered arrangement. The Ga—Ga bond length is 2.392 (1) Å. The other complexes have similar values: 2.406 (1) Å for L = dioxane, 2.403 (1) Å for L = pyridine, 2.421 Å for L = trimethylamine and 2.415 (2) Å for L = 4-methylpyridine. The corresponding Ga—Ga distance in $Ga_2Cl_6^{2-}$ is 2.390 (2) Å.

The Ga—O—P angle of 150.0 (3)° deviates considerably from linearity in contrast to $GaCl_3\cdot$TPPO (TPPO is triphenylphosphine oxide; Burford *et al.*, 1990), where the arrangement is linear; however, in this case, the O-atom displacement parameter indicates that disorder is present, which would imply some degree of non-linearity. The Ga—O distance is 1.881 (4) Å, which is similar to that found for $GaCl_3\cdot$TPPO [1.818 (10) Å]. The torsion angle about the Ga—O bond is 176.9 (6)°, giving a staggered arrangement about this bond.

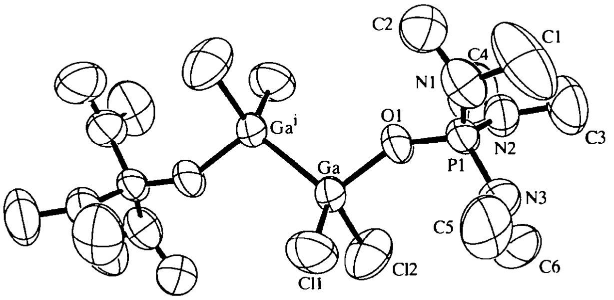


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. Only one of the two half-weighted C atoms (C2) is shown. H atoms have been omitted for clarity.

Experimental

The title compound was prepared directly from gallium metal used as the sacrificial anode of a cell in which the electrolyte was 10 ml of acetonitrile solution containing 0.5 ml of concentrated hydrochloric acid and 0.186 g of hexamethylphosphoramide. Electrolysis, with a current of 10–25 mA, took place for 5 h, during which time hydrogen was evolved from the platinum cathode and the gallium anode underwent a weight loss of 0.801 g. Tests for reducing power by removing small samples of the solution into aqueous $AgNO_3$ showed that a low-valent product was being formed. Following electrolysis, the solution was filtered and evaporated under

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