N1*C*	0.4184 (2)	0.7666 (5)	0.5131 (2)	0.0573 (12)
C1*C*†	0.4597 (4)	0.6985 (10)	0.4735 (4)	0.083 (3)
C1*D*‡	0.4747 (12)	0.771 (3)	0.5404 (14)	0.083 (3)
C2*C*	0.5174 (3)	0.6826 (8)	0.5073 (4)	0.103 (3)
C3*C*†	0.4400 (4)	0.9044 (9)	0.5131 (5)	0.084 (3)
C3*D*‡	0.3873 (12)	0.868 (3)	0.5521 (15)	0.084 (3)
C4*C*	0.4053 (4)	0.9981 (8)	0.5372 (4)	0.112 (3)
C5*C*†	0.3602 (4)	0.7575 (10)	0.4796 (5)	0.085 (3)
C5*D*‡	0.4050 (11)	0.777 (3)	0.4387 (14)	0.085 (3)
C6*C*	0.3471 (3)	0.7963 (8)	0.4093 (4)	0.102 (3)
C7*C*†	0.4250 (5)	0.7259 (12)	0.5832 (5)	0.101 (4)
C7*D*‡	0.3931 (14)	0.638 (4)	0.5324 (14)	0.101 (4)
C8*C*	0.4043 (5)	0.6008 (9)	0.5973 (5)	0.163 (5)
O1*W*	0.3527 (2)	0.2731 (4)	0.3832 (2)	0.0769 (13)
O2*W*	0.2465 (2)	0.5821 (6)	0.4957 (3)	0.129 (2)
O3*W*	0.1670 (2)	0.0688 (5)	0.1911 (3)	0.120 (2)
O4*W*	0.2846 (2)	0.6783 (8)	−0.0195 (2)	0.157 (3)

† Occupancy = 0.75.
‡ Occupancy = 0.25.

Table 2. *Selected geometric parameters* (Å, °)

Eu1—O13	2.438 (3)	Eu2—O33	2.424 (3)
Eu1—O11	2.441 (3)	Eu2—O23	2.434 (3)
Eu1—O21	2.463 (3)	Eu2—O31	2.460 (3)
Eu1—N11	2.540 (4)	Eu2—N31	2.541 (4)
Eu1—N21*A*	2.556 (5)	Eu2—N21*B*	2.560 (5)
O13—Eu1—O11	126.84 (12)	O33—Eu2—O23	81.93 (12)
O13—Eu1—O21	86.08 (12)	O33—Eu2—O31	127.07 (12)
O11—Eu1—O21	80.29 (11)	O23—Eu2—O31	81.37 (11)
O13—Eu1—N11	63.60 (12)	O33—Eu2—N31	64.15 (12)
O11—Eu1—N11	63.33 (12)	O23—Eu2—N31	70.87 (12)
O21—Eu1—N11	71.44 (12)	O31—Eu2—N31	62.92 (11)
O13—Eu1—N21*A*	72.78 (8)	O33—Eu2—N21*B*	72.98 (9)
O11—Eu1—N21*A*	138.25 (8)	O23—Eu2—N21*B*	63.13 (8)
O21—Eu1—N21*A*	63.35 (8)	O31—Eu2—N21*B*	137.26 (8)
N11—Eu1—N21*A*	117.90 (9)	N31—Eu2—N21*B*	120.02 (8)

The asymmetric unit of the crystal structure comprises two halves, each containing two independent molecules with the metal atoms on crystallographic twofold axes. During refinement of the structure, the H atoms in the anions and cations were fixed at estimated positions with $U_{\rm iso}$(H) set at $1.5U_{\rm eq}$(C). The H atoms of the water molecules were located from difference syntheses and were not refined by the least-squares procedure.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *PROFIT* (Streltsov & Zavodnik, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1983). Software used to prepare material for publication: *SHELXL*93.

We gratefully acknowledge partial support of this work by the Australian Research Council.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1151). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Zinc(II) Chloride–Methanol Complex of 2-[(1,3-Dihydro-1,3-dioxo-2*H*-inden-2-ylidene)amino]-1*H*-indene-1,3(2*H*)-dionate(1−) Sodium Salt: a Complex of Ruhemann's Purple

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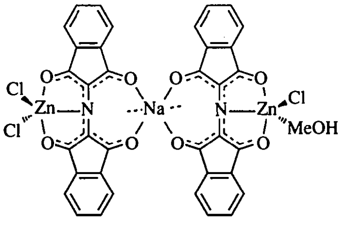
Abstract

The title compound, sodium dichloro{2-[(1,3-dihydro-1,3-dioxo-2*H*-inden-2-ylidene)amino]-1*H*-indene-1,3(2*H*)-dionato(1−)}zincate chloro{2-[(1,3-dihydro-1,3-dioxo-2*H*-inden-2-ylidene)amino]-1*H*-indene-1,3(2*H*)-dionato(1−)}(methanol)zinc, $Na\{[ZnCl_2(C_{18}H_8NO_4)][ZnCl(C_{18}H_8NO_4)(CH_3OH)]\}$, is a linear polymer in the solid state. The Na^+ ion lies on an inversion centre and is octahedrally coordinated to four keto O atoms, two from each dionate ligand [Na···O 2.280 (3) and 2.286 (4) Å] and to two Cl atoms of adjacent moieties [Na···Cl

2.893 (2) Å]. The unique Zn atom has disordered five-fold coordination *via* a tridentate organic ligand [Zn—O 2.196 (3), 2.215 (3), Zn—N 2.109 (3) Å] and either two Cl atoms Zn—Cl [2.205 (2), 2.399 (8) Å], or a Cl atom [Zn—Cl 2.205 (2) Å] and a methanol O atom [Zn—O 1.88 (2) Å]. The complex only fluoresces weakly, which is surprising in view of the fact that the two indandione moieties of each ligand are closer to being coplanar [mean tilt angle = 6.5 (2)°] than in a related cadmium(II) complex (tilt angle = 19.5°) that fluoresces more strongly.

Comment

The formation of this complex represents an attempt to simulate the chemistry that occurs when a latent fingerprint on an absorbent surface is visually enhanced using ninhydrin, which produces the intensely coloured compound known as Ruhemann's purple (RP), and is subsequently further enhanced by spraying with a solution of zinc(II) chloride. Spraying with zinc chloride has been known for some time to produce a fluorescent complex (Herrod & Menzel, 1982) and it is this property that can be made use of in detecting the presence and details of very weak fingerprints. The chemistry of this process, however, is poorly reproducible (Kobus, Stoilovic & Warrener, 1983) and it was felt that knowledge of the structure of the complex, (I), may indicate measures that could be taken to improve the method.



(I)

The complex consists of two five-coordinate Zn^{II} ions each bound by tridentate RP, but with one Zn^{2+} ion binding two Cl^- ions and the other binding one Cl^- ion and a coordinated molecule of methanol. The two half-units are linked by an Na^+ ion coordinating intramolecularly to the two exposed keto groups of each half-unit and intermolecularly to two Cl^- ions. Geometric parameters about Zn and Na are within the usual ranges except that the Zn—Cl2 distance is longer than usual (Table 2). This may be related to disorder on the Cl2 site. The structure of a related six-coordinate mono-cadmium(II) complex has already been determined (Lennard, Margot, Sterns & Warrener, 1987). The Cd^{II} complex is strongly fluorescent (Stoilovic, Kobus, Warrener & Margot, 1986), whereas the Zn complex described here is only weakly fluorescent. This is surprising since it is believed that the fluorescence intensity would increase as the two indandione moieties in each RP ligand approach planarity (Menzel, Bartsch & Hallman, 1990). The approach to planarity is measured by a decreasing tilt angle between the two moieties, which is 19.5° for the Cd complex and 6.5 (2)° for the zinc complex. From the structure of the title compound, it is clear that the Na^+ ion will play a role in determining the tilt angle. As this cation varies with the nature of the surface on which the fingerprint-enhancing chemistry is carried out, and if there is a connection between the tilt angle and the level of fluorescence, it is possible that cation dependency of the tilt angle is the origin of the irreproducible observations (Davies, Kobus, Taylor & Wainwright, 1995).

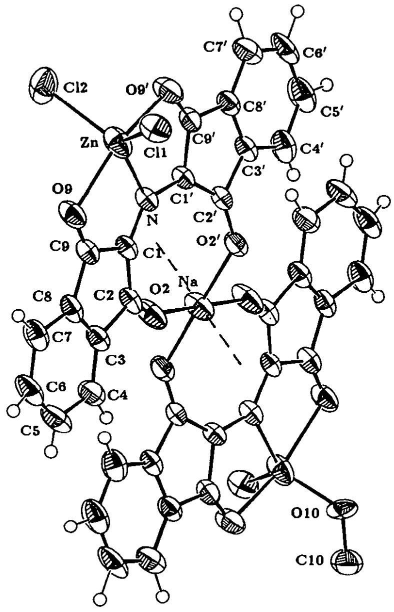


Fig. 1. A view of the molecule with displacement ellipsoids drawn at the 50% probability level; H atoms are drawn as circles of arbitrary radii, those of the methanol molecule are omitted. Octahedral coordination of Na is completed by two Cl1 atoms from adjacent molecules (dashed lines). Na is at a centre of symmetry so that methanol (O10, C10) and Cl2 are mutually disordered.

Experimental

The compound was precipitated by the vapour diffusion of diethyl ether into the reaction mixture arising from the interaction of the sodium salt of Ruhemann's purple with zinc(II) chloride (1:1 molar ratio), carried out in a 5:1 chloroform/methanol mixture. The crystal density D_m was measured by flotation in a 1,1,1-trichloroethane/1,2-dibromoethane mixture.

Crystal data

$Na\{[ZnCl_2(C_{18}H_8NO_4)]$-
$[ZnCl(C_{18}H_8NO_4)$-
$(CH_3OH)]\}$
$M_r = 896.63$
Triclinic
$P\overline{1}$

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 6 reflections
$\theta = 13.16$–20.81°
$\mu = 1.70\ mm^{-1}$

$a = 12.060\,(3)$ Å
$b = 10.027\,(8)$ Å
$c = 8.046\,(2)$ Å
$\alpha = 76.36\,(5)°$
$\beta = 89.08\,(2)°$
$\gamma = 66.09\,(4)°$
$V = 860.9\,(8)$ Å^3
$Z = 1$
$D_x = 1.73$ Mg m^{-3}
$D_m = 1.71\,(1)$ Mg m^{-3}

$T = 293$ K
Sickle-shaped shard
$0.8 \times 0.15 \times 0.15$ mm
Orange

Data collection

CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3114 measured reflections
3024 independent reflections
2537 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.026$
$\theta_{\rm max} = 24.98°$
$h = -14 \rightarrow 14$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 9$
6 standard reflections
frequency: 50 min
intensity decay: <1%

Refinement

Refinement on F
$R = 0.048$
$wR = 0.041$
$S = 3.624$
2533 reflections
259 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{\rm max} = 0.02$
$\Delta\rho_{\rm max} = 0.636$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.635$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
Zn	0.28576 (7)	0.52127 (7)	0.28777 (8)	0.0546 (7)
Cl1	0.2466 (1)	0.4714 (2)	0.0482 (2)	0.056 (1)
Na	0	1/2	1	0.050 (3)
C1	0.0868 (4)	0.6525 (5)	0.4887 (6)	0.036 (4)
C2	−0.0103 (4)	0.7174 (5)	0.5963 (6)	0.039 (5)
O2	−0.0274 (3)	0.6685 (3)	0.7415 (4)	0.057 (4)
C3	−0.0850 (4)	0.8746 (5)	0.4913 (6)	0.039 (5)
C4	−0.1911 (5)	0.9786 (5)	0.5319 (7)	0.049 (5)
C5	−0.2419 (5)	1.1220 (6)	0.4151 (8)	0.058 (6)
C6	−0.1865 (5)	1.1543 (5)	0.2698 (7)	0.057 (6)
C7	−0.0808 (5)	1.0502 (5)	0.2296 (6)	0.050 (5)
C8	−0.0300 (5)	0.9061 (5)	0.3443 (6)	0.040 (5)
C9	0.0798 (5)	0.7714 (5)	0.3372 (6)	0.039 (5)
O9	0.1528 (3)	0.7575 (3)	0.2288 (4)	0.050 (4)
N	0.1796 (3)	0.5198 (4)	0.4985 (5)	0.037 (4)
C1′	0.2186 (4)	0.3821 (5)	0.6098 (6)	0.034 (4)
C2′	0.1726 (4)	0.3096 (5)	0.7566 (6)	0.034 (5)
O2′	0.0734 (3)	0.3533 (3)	0.8107 (4)	0.046 (4)
C3′	0.2718 (4)	0.1564 (5)	0.8201 (6)	0.037 (5)
C4′	0.2747 (5)	0.0460 (6)	0.9617 (7)	0.052 (6)
C5′	0.3763 (6)	−0.0905 (6)	0.9928 (8)	0.063 (6)
C6′	0.4689 (5)	−0.1154 (5)	0.8876 (8)	0.062 (6)
C7′	0.4658 (5)	−0.0042 (6)	0.7431 (7)	0.052 (6)
C8′	0.3644 (4)	0.1331 (5)	0.7142 (6)	0.039 (5)
C9′	0.3324 (4)	0.2708 (5)	0.5741 (6)	0.039 (5)
O9′	0.3888 (3)	0.2899 (3)	0.4492 (4)	0.054 (4)
O10†	0.418 (1)	0.572 (2)	0.304 (3)	0.05 (1)
C10†	0.518 (1)	0.508 (1)	0.193 (2)	0.07 (1)
Cl2†	0.4672 (5)	0.559 (1)	0.325 (1)	0.070 (6)

† Occupancy = 0.5.

Table 2. *Selected geometric parameters* (Å, °)

Zn—Cl1	2.205 (2)	Zn—Cl2	2.399 (8)
Zn—O9	2.196 (3)	Na···Cl1$^{\rm i}$	2.893 (2)
Zn—N	2.109 (4)	Na···O2	2.280 (3)
Zn—O9′	2.215 (3)	Na···O2′	2.286 (4)
Zn—O10	1.88 (2)		
Cl1—Zn—O9	97.2 (1)	N—Zn—O9′	78.7 (1)
Cl1—Zn—N	123.4 (1)	N—Zn—O10	118.0 (7)
Cl1—Zn—O9′	100.4 (1)	N—Zn—Cl2	117.0 (3)
Cl1—Zn—O10	118.6 (7)	O9′—Zn—O10	92.0 (5)
Cl1—Zn—Cl2	119.3 (3)	O9′—Zn—Cl2	86.0 (2)
O9—Zn—N	78.7 (1)	O2—Na···Cl1$^{\rm i}$	90.1 (1)
O9—Zn—O9′	156.5 (1)	O2′—Na···Cl1$^{\rm i}$	85.8 (1)
O9—Zn—O10	93.0 (5)	O2—Na···O2′	75.7 (1)
O9—Zn—Cl2	98.8 (2)		

Symmetry code: (i) $x, y, 1 + z$.

The structure was solved by a combination of Patterson and Fourier techniques. Several models with different interpretations of the positions of Cl2 and the methanol ligand were refined: (1) in $P1$ with ordered ligands; (2) in $P1$ with Cl2 and methanol on both Zn atoms of the unit cell with variable population parameters; (3) similar to (2) in $P\bar{1}$. (1) and (2) resulted in unrealistic displacement parameters for many of the RP atoms and significantly higher R values than (3). The population parameters in (3) refined to values that were not significantly different from 0.5. The coordinates reported herein are the result of a refinement in $P\bar{1}$ with fixed population parameters of 0.5 for methanol and Cl2 atoms. It is likely that every molecule is of the form shown in Fig. 1. The model suggests that the crystals may consist of ordered domains, within which the true space group is $P1$, separated by antiphase boundaries. The size of the domains is unknown. Between molecules within a domain there is the possibility of a weak hydrogen bond from methanol O10 to Cl2 of an adjacent molecule [O10···Cl2 3.05 (2) Å]. H atoms of methanol could not be located in difference maps and were not included in the model.

Data reduction: *DIFDAT*, *ADDREF*, *SORTRF* in *Xtal* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *FOURR*, *PEKPIK*, *MODEL* in *Xtal*. Program(s) used to refine structure: *CRYLSQ* in *Xtal*. Molecular graphics: *ORTEP*II (Johnson, 1976) in *Xtal*. Software used to prepare material for publication: *BONDLA*, *CIFIO* in *Xtal*.

The authors are very grateful to Associate Professor A. H. White of The University of Western Australia for collecting the data.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraethylammonium Salt of *trans*-Bis(acetonitrile)tetrachlororuthenate(III), a Notable Optical Chromophore

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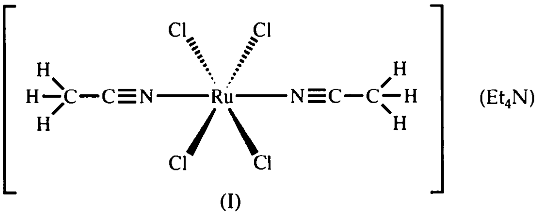
Abstract

In accord with its optical and electrochemical properties, the complex anion of the title compound, *trans*-[$(C_2H_5)_4N$][$RuCl_4(C_2H_3N)_2$], displays almost perfect tetragonal symmetry, with *trans*-linear MeCN coordination.

Comment

Tetraethylammonium *trans*-bis(acetonitrile)tetrachlororuthenate(III), (I), is an important member of an extended substitutional series with the general formula $[Ru^{III}Cl_{6-n}(MeCN)_n]^{n-3}$ (n = 1–6) under examination in our laboratory. This family shows very orderly progressions in metal-centered electrode potentials and charge-transfer spectra as a function of stoichiometry and structure, and so provides a means of testing conflicting electronic theories of ligand additivity (Duff & Heath, 1991*a*). We described recently the molecular geometry of the benzonitrile complexes *trans*-$[RuCl_4(PhCN)_2]^-$ and *mer*-$[RuCl_3(PhCN)_3]$ (Duff, Heath & Willis, 1990) and now extend our studies to include the corresponding acetonitrile compound *trans*-$[RuCl_4(MeCN)_2]^-$, (I).



(I)

This compound constitutes a most instructive tetragonal MX_4L_2 chromophore, due in part to the exceptional redox inertness and UV-transparency of acetonitrile ligands (even when compared with PhCN). The UV/visible spectrum of (I) reveals a well defined set of charge-transfer bands spanning $Cl(\pi/\sigma)$ to $Ru(d_{xy})$ and to $Ru(d_{x^2-y^2})$ (Duff & Heath, 1991*b*). There is also the prospect of locating the direct tetragonal crystal-field transition (d_{xz}, $d_{yz} \rightarrow d_{xy}$) which is known only in the 5*d* osmium analogue (Heath & Humphrey, 1991). The present structure determination opens the way for detailed single-crystal optical and EPR measurements to examine these assignments.

The X-ray analysis of the title compound reveals discrete well defined $[RuCl_4(MeCN)_2]^-$ anions and $[Et_4N]^+$ cations, with both ions occupying special positions. As expected, the pertinent bond lengths observed for the anion in (I) resemble those in the PhCN analogue, where the mean measured values are Ru—Cl 2.353, Ru—N 2.013 and N—C 1.130 Å and Ru—N—C 176.1°. The inner coordination sphere closely approximates true tetragonal geometry though only a centre of symmetry is crystallographically imposed on the molecule. Thus the Ru—Cl(1) and Ru—Cl(2) bonds are experimentally indistinguishable, and the *cis*-Cl—Ru—Cl and Cl—Ru—N angles approach 90°, within 1.0 and 1.5°, respectively. The MeCN moiety is virtually linear within experimental error [N—C—C 179.1 (5)°] and tilted only slightly (but measurably) from collinearity with Ru [Ru—N—C 177.0 (4)°].

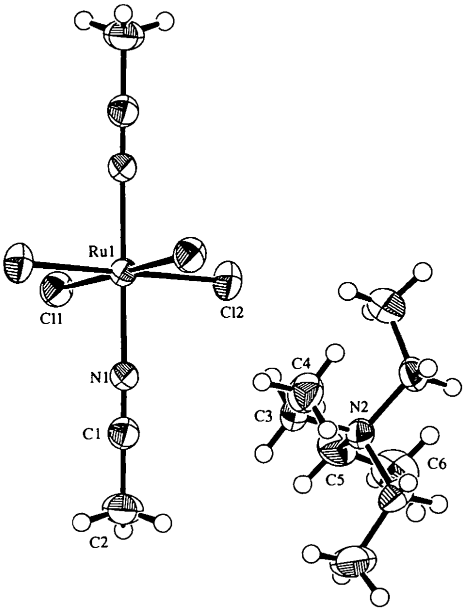


Fig. 1. View of (I) showing the labelling of all unique non-H atoms. Displacement ellipsoids are shown at 50% probability levels. H atoms are drawn as circles of arbitrary radii.

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