Data collection: *P3/P4-PC* (Siemens, 1991). Cell refinement: *P3/P4-PC*. Data reduction: *XDISK* in *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL-Plus*. Program(s) used to refine structure: *XLS* in *SHELXTL-Plus*. Molecular graphics: *XP* in *SHELXTL-Plus*. Software used to prepare material for publication: *XPUBL* in *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71805 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1080]

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A Tri-μ-chloro Dirhodium(III) Complex $[Rh_2(\mu\text{-}Cl)_3(triphos)_2](CF_3SO_3)_3$ [triphos = $CH_3C(CH_2PPh_2)_3$]

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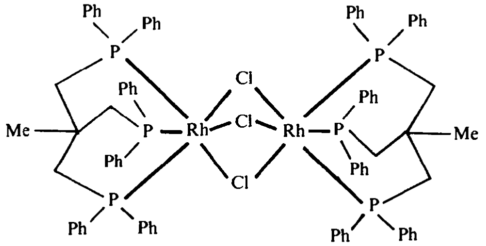
Abstract

The crystal structure of tri-μ-chloro-bis({2-[(diphenylphosphino)methyl]-2-methyl-1,3-propanediyl}bis(diphenylphosphine)-*P*,*P'*,*P''*)dirhodium(III) tris(trifluoromethanesulfonate), $[Rh_2(\mu\text{-}Cl)_3(triphos)_2](CF_3SO_3)_3$, where triphos is the tripod-like tridentate ligand $CH_3C(CH_2PPh_2)_3$, has been determined by X-ray diffraction. The tri-cationic complex $[Rh_2(\mu\text{-}Cl)_3(triphos)_2]$ has a distorted cofacial bioctahedral geometry with two Rh atoms sharing a triangular face formed by three bridging Cl atoms. It is characterized by a long Rh···Rh distance of 3.414 (4) Å and by a consequent elongation of the coordination polyhedron. The coordination geometry is also distorted by a 34° rotation of both [(triphos)Rh] units around the *M*···*M* direction.

Comment

In the course of studies of the reactivity of the Rh^{III} complex $[RhCl_3(triphos)]$, where triphos is the tripod-like tridentate ligand $CH_3C(CH_2PPh_2)_3$, a number of mono- and polynuclear compounds were obtained, depending on the reaction conditions and the ratio of reagents. Some of the products display diverse and novel structural properties. One of them, the di-μ-chloro complex $[Rh_2Cl_2(\mu\text{-}Cl)_2(triphos)_2]^{2+}$ was found to form in a methanol solution of $[RhCl_3(triphos)]$ and then to react slowly yielding the tri-μ-chloro complex $[Rh_2(\mu\text{-}Cl)_3(triphos)_2]^{3+}$, (1) (Ott, 1986). This latter reaction occurred under the crystallization conditions, as the X-ray analysis showed.



(I)

The crystal structure of the title compound consists of discrete $[Rh_2(\mu\text{-}Cl)_3(triphos)_2]^{3+}$ cations and $(CF_3SO_3)^-$ anions with no short contacts between atoms of different ions. A perspective view of the cation is shown in Fig. 1.

Each Rh atom is octahedrally coordinated by the three P atoms of the triphos ligand and by the three bridging Cl atoms. The two octahedra share the face formed by the Cl atoms to form a cofacial bioctahedral polyhedron. The elongation axis of the polyhedron lies on the threefold axis of the cubic cell. Thus the whole complex has crystallographic C_{3v} symmetry and only one third of it is symmetry independent (Fig. 2).

The geometry of the cofacial bioctahedron presents severe distortions. The two [(triphos)Rh] units are rotated around the Rh···Rh direction by 34.0 (2)° with respect to each other. As a result of this rotation each P atom does not lie on the plane defined by Rh(1), Rh(2) and its Cl_{trans} atom, but is rotated away from the plane, by 16° for the P atoms of the [(triphos)Rh(1)] unit and by −18° for those of the [(triphos)Rh(2)] unit (Fig. 3). This type of distortion has been found in two other triphos complexes: $[Fe_2(\mu\text{-}H)_3(triphos)_2]^+$ and $[Co_2(\mu\text{-}H)_3(triphosAs)_2]^+$ (Dapporto,

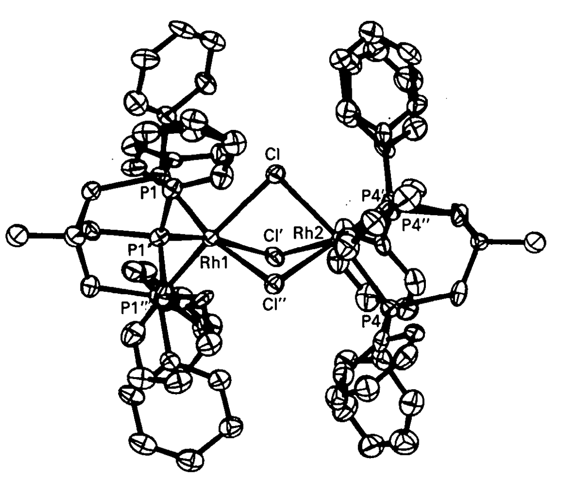


Fig. 1. Perspective view of the cationic complex. Displacement ellipsoids are shown at the 50% probability level.

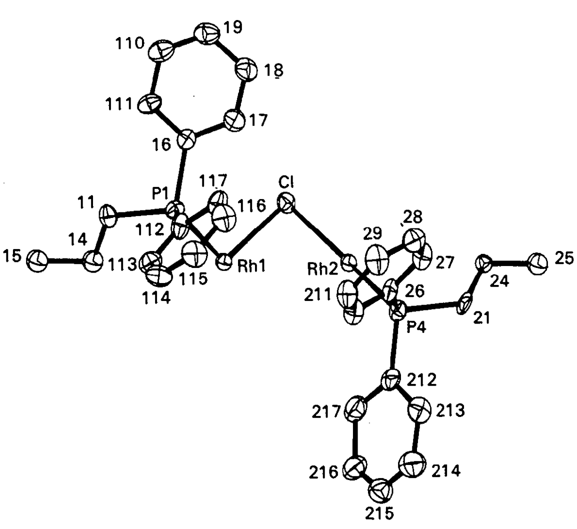


Fig. 2. The asymmetric part of the cationic complex.

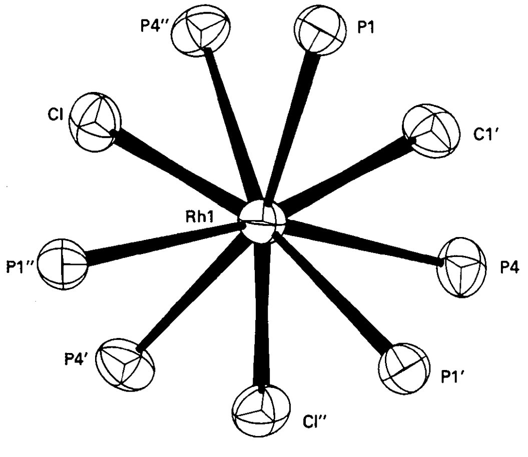


Fig. 3. View of the complex core down the Rh···Rh direction.

Midollini & Sacconi, 1975). In both cases, because of the short $M\cdots M$ distance [Fe···Fe = 2.332 (3) and Co···Co = 2.377 (8) Å], steric repulsions among the phenyl groups of the two units may engender the rather large torsion angles around the $M\cdots M$ direction [15° in the Fe complex and 18–21° in the Co complex]. In the case of (1), steric hindrance between the triphos ligands is unlikely to be responsible for the twist around the Rh···Rh direction. In addition, in the analogous Ru^{II} complex $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]^+$, (2), with Ru···Ru = 3.445 (1) Å, the [(triphos)Ru] units are exactly eclipsed (Rhodes, Sorato, Venanzi & Bachechi, 1988).

The coordination polyhedron is also very elongated with respect to the ideal geometry; the internal angles reflect this type of distortion. The three Rh—Cl—Rh angles of 87.3 (1)° are much larger than the ideal value of 70.5° and the six Cl—Rh—Cl angles, 77.8 (1)° about Rh(1) and 77.4 (1)° about Rh(2), are smaller than the ideal value of 90°. The same type of distortion is generally found, though to a different degree, in Rh and Ru tri-μ-chloro complexes since the metals are further apart than they would be in a regular face-sharing bioctahedron.

The Rh···Rh distance of 3.414 (4) Å is much longer than those found in similar Rh complexes, such as $[Rh_2(\mu\text{-}Cl)_3(COCH_3)_2(PMe_2Ph)_4]^+$ [3.3284 (6) Å (Bennett, Jeffery & Robertson, 1981)], $[Rh_2(\mu\text{-}Cl)_3Cl_3(P\text{-}{}^nBu_3)_3]$ [3.187 (4) Å (Muir, Barretty & Muir, 1976)] and $[Rh_2(\mu\text{-}Cl)_3Cl_6(Me_3PhN)_3]$ [3.121 (5) Å (Cotton & Ucko, 1972)]. It is comparable to the Ru^{II}···Ru^{II} distance [3.455 (1) Å] of the analogous triphos complex (2) and to those in $[Ru_2(\mu\text{-}Cl)_3(PMe_2Ph)_6]^+$ [3.39 (1) Å (Laing & Pope, 1976)] and $[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]^+$ [3.443 (4) Å (Raspin, 1969)], which in turn are exceptionally long. In some recent determinations, short values such as 3.236 (1) Å in $[Ru_2(\mu\text{-}Cl)_3(DMSO)_5Cl]$ (Calligaris, Faleschini & Alessio, 1993) and 3.35 Å in $[Ru_2(\mu\text{-}Cl)_3(dppb)_2(DMSO)]$ [where dppb = 1,4-bis(diphenylphosphino)butane] (Joshi, Thorburn, Retting & James, 1992) have been found.

Experimental

Crystal data

$[Rh_2Cl_3(C_{41}H_{39}P_3)_2]$-
$(CF_3SO_3)_3$
M_r = 2008.7
Cubic
$Pa\overline{3}$
a = 26.430 (6) Å
V = 18462 (7) Å^3
Z = 8
D_x = 1.448 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 14.0–18.0°
μ = 0.6751 mm^{-1}
T = 295 K
Prism
0.5 × 0.3 × 0.2 mm
Yellow

Data collection

Syntex $P2_1$ diffractometer
Profile data from ω scans

R_{int} = 0.0153
$\theta_{\max}$ = 28.0°

Absorption correction:
empirical with ψ scan at $\chi = 90°$
$T_{\min} = 0.78$, $T_{\max} = 1.00$
6681 measured reflections
3893 independent reflections
1782 observed reflections
$[I > 3\sigma(I)]$

$h = 0 \rightarrow 26$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 26$
3 standard reflections
monitored every 100 reflections
intensity variation: 8.0%

Refinement

Refinement on F
$R = 0.0680$
$wR = 0.0759$
$S = 4.12$
1782 reflections
346 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.90$

$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2A, 2.3.1 for C, O, F, P, S, Cl, Rh; Table 2.2C for H)

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

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

	x	y	z	$U_{\rm eq}$
Rh(1)	0.2219 (1)	x	x	0.034 (1)
Rh(2)	0.2965 (1)	x	x	0.035 (1)
C(14)	0.1435 (8)	x	x	0.05 (1)
C(15)	0.1101 (8)	x	x	0.06 (1)
C(24)	0.3773 (8)	x	x	0.05 (1)
C(25)	0.4094 (8)	x	x	0.06 (1)
P(1)	0.2110 (2)	0.1352 (2)	0.2314 (2)	0.041 (2)
P(4)	0.3824 (2)	0.3105 (2)	0.2856 (2)	0.045 (2)
Cl(1)	0.2123 (2)	0.2568 (2)	0.3080 (2)	0.045 (2)
C(11)	0.1627 (7)	0.1083 (7)	0.1870 (7)	0.05 (1)
C(16)	0.1917 (6)	0.1117 (6)	0.2946 (7)	0.04 (1)
C(17)	0.2139 (8)	0.1312 (8)	0.3388 (8)	0.07 (1)
C(18)	0.203 (1)	0.1155 (9)	0.3860 (8)	0.07 (1)
C(19)	0.169 (1)	0.0745 (9)	0.391 (1)	0.07 (1)
C(110)	0.149 (1)	0.0538 (9)	0.350 (1)	0.08 (1)
C(111)	0.1609 (7)	0.0705 (7)	0.3006 (8)	0.06 (1)
C(112)	0.2700 (7)	0.0991 (7)	0.2182 (9)	0.06 (1)
C(113)	0.3051 (7)	0.0911 (8)	0.2581 (8)	0.06 (1)
C(114)	0.3504 (9)	0.0676 (9)	0.247 (1)	0.07 (1)
C(115)	0.3612 (8)	0.0516 (9)	0.200 (1)	0.07 (1)
C(116)	0.3287 (7)	0.0581 (8)	0.162 (1)	0.07 (1)
C(117)	0.2818 (7)	0.0817 (7)	0.1704 (9)	0.07 (1)
C(21)	0.4074 (8)	0.3578 (7)	0.3323 (8)	0.05 (1)
C(26)	0.4190 (7)	0.2518 (7)	0.2933 (9)	0.05 (1)
C(27)	0.4414 (7)	0.2408 (8)	0.3391 (9)	0.06 (1)
C(28)	0.4680 (8)	0.1942 (9)	0.3442 (9)	0.07 (1)
C(29)	0.4728 (8)	0.1622 (9)	0.305 (1)	0.08 (1)
C(210)	0.4532 (7)	0.1734 (8)	0.2609 (9)	0.07 (1)
C(211)	0.4260 (8)	0.2197 (8)	0.2535 (9)	0.07 (1)
C(212)	0.4077 (9)	0.3320 (7)	0.2262 (9)	0.06 (1)
C(213)	0.4600 (8)	0.3399 (8)	0.218 (1)	0.07 (1)
C(214)	0.478 (1)	0.357 (1)	0.170 (1)	0.09 (2)
C(215)	0.454 (1)	0.363 (1)	0.131 (2)	0.08 (1)
C(216)	0.408 (2)	0.359 (1)	0.135 (1)	0.08 (2)
C(217)	0.3796 (9)	0.3409 (9)	0.183 (1)	0.08 (1)
S(1)	0.0249 (3)	0.0232 (3)	0.2588 (3)	0.085 (3)
C(42)	−0.012 (1)	−0.000 (1)	0.210 (1)	0.09 (1)
O(1)	0.0562 (6)	0.0573 (6)	0.2306 (7)	0.09 (1)
O(2)	−0.0104 (7)	0.0453 (8)	0.2935 (9)	0.13 (1)
O(3)	0.0489 (7)	−0.0207 (7)	0.2808 (8)	0.11 (1)
F(1)	−0.0408 (6)	0.0336 (7)	0.1861 (7)	0.12 (1)
F(2)	0.0111 (8)	−0.0252 (7)	0.1737 (7)	0.14 (1)
F(3)	−0.0458 (8)	−0.0360 (8)	0.2272 (8)	0.16 (1)

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

Rh(1)—Rh(2)	3.414 (1)	P(4)—C(21)	1.87 (2)
Rh(1)—P(1)	2.321 (5)	P(4)—C(26)	1.84 (1)
Rh(1)—Cl(1)	2.469 (5)	P(4)—C(212)	1.79 (2)
Rh(2)—P(4)	2.319 (4)	C(14)—C(15)	1.52 (2)
Rh(2)—Cl(1)	2.478 (5)	C(14)—C(11)	1.56 (2)
P(1)—C(11)	1.87 (1)	C(24)—C(25)	1.46 (2)
P(1)—C(16)	1.85 (1)	C(24)—C(21)	1.52 (2)
P(1)—C(112)	1.86 (2)		
Rh(1)—Cl(1)—Rh(2)	87.3 (1)	C(212)—P(4)—C(21)	103.4 (9)
Cl(1)—Rh(1)—Cl(1′)	77.8 (1)	C(212)—P(4)—C(26)	99.5 (9)
Cl(1)—Rh(2)—Cl(1′)	77.4 (1)	C(11)—C(14)—C(15)	105 (1)
P(1)—Rh(1)—P(1′)	89.9 (1)	P(1)—C(11)—C(14)	117 (1)
P(1)—Rh(1)—Cl(1)	104.8 (2)	C(17)—C(16)—P(1)	120 (1)
P(1)—Rh(1)—Cl(1′)	88.4 (1)	C(111)—C(16)—P(1)	122 (1)
P(1)—Rh(1)—Cl(1″)	165.2 (1)	C(113)—C(112)—P(1)	118 (1)
P(4)—Rh(2)—P(4′)	89.1 (1)	C(117)—C(112)—P(1)	122 (1)
P(4)—Rh(2)—Cl(1)	164.2 (2)	C(21)—C(24)—C(25)	110 (1)
P(4)—Rh(2)—Cl(1′)	88.3 (1)	P(4)—C(21)—C(24)	123 (1)
P(4)—Rh(2)—Cl(1″)	106.5 (1)	C(27)—C(26)—P(4)	119 (1)
C(16)—P(1)—C(11)	104.5 (8)	C(211)—C(26)—P(4)	120 (1)
C(112)—P(1)—C(11)	104.8 (9)	C(213)—C(212)—P(4)	123 (1)
C(112)—P(1)—C(16)	103.1 (9)	C(217)—C(212)—P(4)	125 (1)
C(26)—P(4)—C(21)	107.7 (9)		
P(1)—Rh(1)—Rh(2)—P(4)	86.0 (2)		
P(1)—Rh(1)—Rh(2)—P(4′)	−156.0 (2)		
P(1)—Rh(1)—Rh(2)—P(4″)	−34.0 (2)		

The crystals were very unstable. The X-ray analysis was carried out on a crystal sealed in a glass capillary with its mother liquor (MeOH/CH_2Cl_2). Absorption correction and linear decay correction factors were applied to all reflections. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods. Non-H atoms were refined anisotropically, except for those in special positions on the three-fold axis. H atoms were included at geometrically idealized positions and allowed to ride on the parent C atoms, except those of the two Me groups. Computer programs included *CAOS* (Cerrini & Spagna, 1977).

The author wishes to thank Professor L. M. Venanzi for providing crystals of the compound and for valuable discussions.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1075). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Monochloroindium Derivative of tmtaa (Dibenzotetramethyltetraaza[14]annulene), $[In(C_{22}H_{22}N_4)Cl]$

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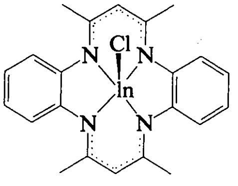
Abstract

The structure consists of an InCl fragment bonded symmetrically to the four N atoms of the macrocyclic ligand tmtaa (chloro{3,5,14,16-tetramethyl-2,6,13,17-tetraazatricyclo[16.4.0.$0^{7,12}$]docosa-1(18),2,5,7(12),8,10,13,16,-19,21-decaenediido-*N,N',N'',N'''*}indium). This is the first structural characterization of an In entity coordinated to this ligand and reveals an unusual five-coordinate square-pyramidal geometry around the In atom. The metal is displaced 0.738 (3) Å above the N_4 coordination plane. The average In—N bond distance is 2.165 (5) Å and the In—Cl distance is 2.380 (2) Å.

Comment

The aim of this investigation was to confirm the expected *mm* symmetry, determine the displacement of the metal ion from the mean plane of the four N atoms of the macrocycle and compare the structure with similar derivatives of this ligand and other porphyrin systems. The molecular structure of the title compound, (I), and atomic labelling scheme are shown in Figs. 1 and 2.



(I)

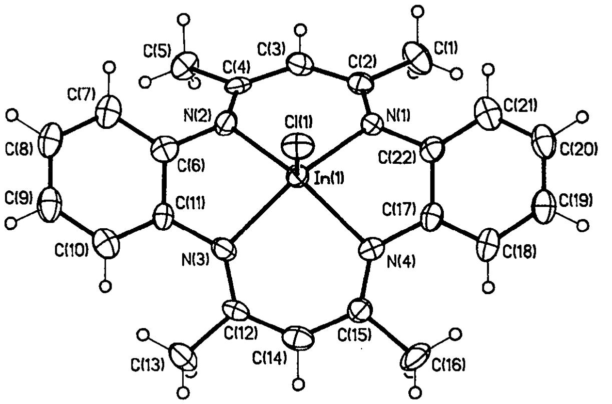


Fig. 1. Face view of [In(tmtaa)Cl] showing the atomic numbering scheme with displacement ellipsoids at 50% probability.

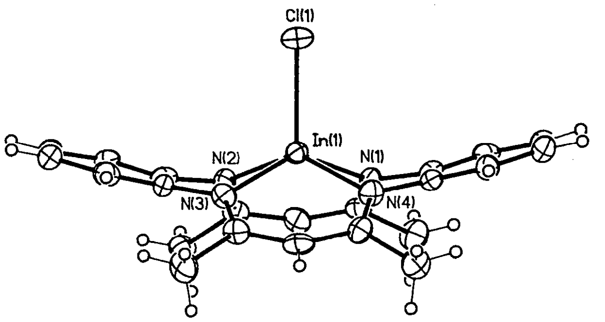


Fig. 2. Side view of [In(tmtaa)Cl] showing the saddle conformation adopted by the ligand.

Fig. 2 shows that the familiar saddle shape, adopted by the free macrocycle and arising from steric interactions between the methyl and phenyl groups, is retained in the metal complex (*cf.* Cotton & Czuchajowska, 1990). The metal is symmetrically bound 0.738 (3) Å above the N_4 plane. This displacement is significantly greater than that found for the Ga derivative (0.48 Å) (Atwood, Atwood, Cowley, Atwood & Román, 1992) and may be explained in terms of the larger covalent radius of In (1.41 Å) with respect to Ga (1.20 Å) (Alcock, 1990). The displacement of In from the N_4 plane is not unexpected, since the nitrogen-to-centre (N—Ct) distance of the dianionic tmtaa ligand lies in the range 1.85-1.87 Å (Weiss, Bursten, Peng & Goedkin, 1976), *i.e.* substantially less than the observed In—N distance [2.165 (5) Å]. As a result of metal coordination, torsional distortions and angle deformations occur in the 14-membered ring to minimize steric interactions, and the N—Ct distance increases to 2.035 Å.

The bond distances for In—Cl [2.380 (2) Å] and In—N [2.165 (5) Å average] are similar to those found in the related structure of tetraphenylporphyrinindium(III) chloride [2.369 (2) and 2.156 (6) Å average, respectively (Ball, Lee, Marshall & Trotter, 1980)]. It has been suggested that the metal-to-axial-group bond distance becomes greater as the charge donation to the metal from the macrocyclic ligand increases (Weiss, Bursten, Peng & Goedkin, 1976). Such charge donation is expected to be significantly larger for the $C_{22}H_{22}N_4^{2-}$ ligand compared