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Syntheses and Crystal Structures of Bis[2-(benzylamino)-4-methylpyridinato]-trichlorotantalum(V) and Bis[2-(benzylamino)-6-methylpyridinato]trichlorotantalum(V)

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The title compounds, bis[2-(benzylamino)-4-methylpyridinato]trichlorotantalum(V) (**1**) and bis[2-(benzylamino)-6-methylpyridine]trichlorotantalum(V) (**2**), were prepared in a melt reaction of corresponding aminopyridine and tantalum(V) chloride. Complex **1** crystallizes from toluene in the monoclinic space group $C2/c$ with unit-cell parameters of $a=10.577(7)$, $(b)=23.018(11)$, $c=11.102(4)$ Å and $\beta=93.35(4)°$ and **2** crystallizes from *p*-xylene in the triclinic space group $P\bar{1}$ with $a=12.113(11)$, $b=14.329(9)$, $c=10.066(7)$ Å, $\alpha=100.51(5)$, $\beta=90.15(7)$ and $\gamma=106.53(5)°$. The atoms of the coordination spheres around the transition metals form pseudo-pentagonal bipyramids. Both **1** and **2** are C_2 symmetric molecules, in **1** this symmetry is also crystallographic with Ta and one Cl atom on a twofold axis. In **2** a tantalum complex and *p*-xylene (1 : 1) solvate form the asymmetric unit.

Among the large number of early transition-metal complexes prepared for olefin polymerization pro-catalysts[1] there are only a few compounds that do not contain cyclopentadienyl ligands. Such compounds are mainly alkoxo[2] and amido complexes, the latter type has been currently under interest. Bis(alkylsilylamido)zirconium chlorides and fluorides have been reported to polymerize ethylene with activities up to 13 kg(PE)/(mol(Zr) h atm),[3] and several aminopyridinato complexes have been introduced as a new alternative catalyst precursors.[4–10] Many of the previously known 2-aminopyridine complexes were dimetallic, such as trichlorotris[2-(phenylamino)pyridinato]diosmium(III)[11] and tetrakis[2-(phenylamino)pyridinato]ditungsten(II).[12] Until 1996 monomeric complexes reported were few: bis[2-(methylamino)pyridinato](tetramethylethylenediamine)-vanadium(II)[13] and bis[2-(methylamino)pyridinato]-bis(triphenylphosphine)rutenium(II).[14] The group of Kempe has recently reported various titanium[4,5] and zirconium[15] complexes that contain mainly silylamino-pyridinato ligands. Whereas several phenyl- and benzyl-aminopyridinato complexes of niobium and tantalum have been prepared in our laboratory.[7–9] We have found that methylaluminoxane-activated tantalum complexes are highly active in ethylene polymerization,[6] e.g. trichlorobis[2,6-di(phenylamino)pyridinato]tantalum(V)[9] had activities of 4900 kg/[mol(Ta) h atm]. Besides the high activity, the tantalum complex yields polymers with a narrow molecular weight distribution.

Experimental

All reaction steps were carried out under an argon atmosphere using standard Schlenk techniques. In both cases a portion of air-sensitive crystals were transferred to perfluoropolyether. The crystal selected for the X-ray measurements was mounted on the glass fibre using the oil-drop method.[16]

Synthesis of [Ta(BzN4MePy)$_2$Cl$_3$] (**1**). Tantalum(V) chloride (1.96 g, 5.47 mmol) and 2-(benzylamino)-4-methylpyridine (2.65 g, 13.4 mmol, m.p. 98–100 °C) were melted at 100°C for 30 min followed by addition of toluene (50 ml) and then refluxed for 2 h. Toluene solution was then filtered and red crystals were obtained overnight.

Synthesis of [Ta(BzN6MePy)$_2$Cl$_3$] (**2**). Tantalum(V) chloride (2.00 g, 5.58 mmol) and 2-(benzylamino)-6-methylpyridine (2.43 g, 12.3 mmol, m.p. 64–66 °C) were heated at 75 °C for 10 min. 70 ml of *p*-xylene were added, and the solution was refluxed for 2 h and filtered through

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Celite. The solution was kept at room temperature, and red crystalline blocks were obtained after 48 h.

X-Ray crystallography. Intensity data were recorded with a Rigaku AFC-7S diffractometer using graphite-monocromatised Mo $K\alpha$ ($\lambda = 0.7173$ Å) radiation using 2θ–ω scans. Intensities of the three standard reflections recorded after every 200 intensity scans showed only minor fluctuations during both data collections. The intensity data were corrected for Lorentz and polarization effects and absorption (ψ-scans) with TEXSAN single-crystal structure analysis software.[17] Structures were solved with the SHELXTL PC 4.1 program package,[18] and refinements with full matrix least-squares on F^2 were carried out with SHELXL93[19] using all collected reflections. In both cases all non-hydrogen atoms were refined anisotropically. In **1** hydrogen atoms were found in the Fourier map and refined, whereas in **2** they were introduced in calculated positions with thermal parameters 1.3 times those of the parent atoms. Crystallographic data are presented in Table 1. Fractional atom coordinates for the complexes are presented in Tables 2 and 3. Structure factors and anisotropic thermal parameters are available from the authors as supplementary material.

Table 1. Crystal data for $[Ta(BzN4MePy)_2Cl_3]$ and $[Ta(BzN6MePy)_2Cl_3]$.

Compound	$[Ta(BzN4MePy)_2Cl_3]$	$[Ta(BzN6MePy)_2Cl_3]$
Formula	$C_{26}H_{26}Cl_3N_4Ta$	$C_{26}H_{26}Cl_3N_4Ta \cdot C_8H_{10}$
Formula mass (g/mol)	681.81	787.97
Colour, Habit	Dark red, Prism	Dark red, Prism
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$, No. 15	$P\bar{1}$, No. 2
Temperature/K	193(1)	193(1)
a/Å	10.577(7)	10.066(7)
b/Å	23.018(11)	12.113(11)
c/Å	11.102(4)	14.329(9)
α/°	90	106.53(6)
β/°	93.35(4)	100.51(5)
γ/°	90	90.15(7)
V/Å^3	2698(2)	1644(2)
Z	4	2
D_c/g cm^{-3}	1.678	1.592
Crystal size/mm	0.4 × 0.4 × 0.3	0.3 × 0.3 × 0.2
$F(000)$	1336	784
μ/mm^{-1}	4.392	3.616
Transmission range	0.8103–1.0000	0.6819–1.0000
2θ range/°	5–50	5–50
Independent reflections	2338	5552
Observed reflections $[F^2 > 2\sigma(F^2)]$ for R	2285	5113
Parameters	207	380
Extinction coefficient	None	0.006(1)
R $[F^2 > 2\sigma(F^2)]$	0.0282	0.0505
wR_2	0.0747	0.1372
S (Goodness of fit, F^2)	1.101	1.087
Residual e-density/e Å^{-3}	1.793 and −2.329	2.644 and −5.243

$R = \Sigma ||F_o| - |F_c|| / |F_o|$ with $F^2 > 2\sigma(F^2)$; the function minimised is $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)]]^{0.5}$. $S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{0.5}$.

Results and discussion

Traditionally, amido complexes of early transition metals have been prepared in reactions of lithiated ligand precursors.[20] In the case of aminopyridines this route is sometimes difficult, for example lithiated 2-(methylamino)pyridine was reported to give chlorotris(methylaminopyridinato)titanium with a very low yield.[5] In our studies only the lithium adduct of 2-(phenylamino)pyridine was isolated when titanium, zirconium and hafnium tetrachlorides were reacted with the butyllithium-treated pro-ligand. However, generalizations cannot be made, because chlorotris[2-(trimethylsilylamino)pyridinato)zirconium[15] was obtained with a good yield via the butyllithium reaction route.

Alternative synthetic methods have improved yields. Kempe *et al.* introduced a sophisticated method which involves an amidoligand exchange: mixed chloro–amido complexes are allowed to react with aminopyridines.[5,15] Dialkylamido ligand, e.g. dimethylamide, behaves as a leaving group. Complexes such as chlorotris[4-(methyl-2-((trimethylsilyl)-amino)pyridine]zirconium[15] and chlorobis[4-methyl-2-((trimethylsilyl)amino)pyridine](dimethylamido)titanium[5] have been prepared by this method. Various interesting aminopyridinato complexes can be obtained; however, the method is not very selective: tris(aminopyridinato) complexes[15] are obtained when bis(dialkylamido) complexes are used. Furthermore, dialkylamide can remain unreacted[5] or behave as a neutral Lewis donor.[21]

We have recently shown that mixed aminopyridinatochloro complexes can be prepared without lithium intermediates in direct reactions.[7–10] Syntheses can be carried out in a high boiling hydrocarbon solvent or even in a melt reaction without solvent. Both ways readily give bis(aminopyridinato) complexes. The methods are particularly practical for niobium(v)[7,8] and tantalum(v).[7–9] Selectivity can be explained with coordinative saturation, tris(aminopyridinato) complexes are not formed if pro-ligand/metal ratios are raised. Both pro-ligands used in the reactions presented here have low melting points, and are therefore most suitable for melt reactions.

Our current interest in tantalum aminopyridinato complexes arises from their activity in polymerization of olefins. Trichlorobis[2,6-di(phenylamino)pyridinato]-tantalum(V) (**3**) and bis[2-(benzylamino)pyridinato]-trichlorotantalum(V) (**4**) activated with methylaluminoxane showed the following activities in ethylene polymerizations: 4900 kg(PE)/[mol(Ta) h atm] and 1000 kg(PE)/[mol(Ta) h atm], respectively.[6] The polydis-

Table 2. Atomic coordinates ($\times 10^4$) equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for [Ta(BzN4MePy)$_2$Cl$_3$].

Atom	$10^4x/a$	$10^4x/b$	$10^4x/c$	10^3U_{eq}[a]/Å^2
Ta	0	1807(1)	7500	22(1)
Cl1	0	2865(1)	7500	33(1)
Cl2	1047(1)	1839(1)	9458(1)	35(1)
N1	1884(3)	2015(2)	6842(3)	28(1)
C2	2140(4)	1451(2)	6582(4)	27(1)
C3	3297(4)	1290(2)	6147(4)	30(1)
C4	4195(4)	1720(2)	5993(4)	32(1)
C4m	5485(5)	1566(3)	5587(5)	42(1)
C5	3905(4)	2297(2)	6263(4)	35(1)
C6	2736(4)	2431(2)	6697(4)	33(1)
N7	1088(3)	1143(1)	6862(3)	27(1)
C8	928(4)	553(2)	6386(4)	28(1)
C9	1769(4)	99(2)	7012(4)	28(1)
C10	1841(5)	−451(2)	6493(5)	42(1)
C11	2615(6)	−879(2)	7024(5)	52(1)
C12	3333(6)	−755(3)	8064(5)	52(1)
C13	3279(6)	−219(2)	8593(5)	46(1)
C14	2487(5)	210(2)	8068(4)	34(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

persity index was narrow in both cases (<2.0).* Simple reasons for the contrasting activities can not be proposed because the complexes are different both in their steric and electronic properties. The present compounds (**1** and **2**) were prepared hoping that explanations for the differences in catalyst behaviour of the aminopyridinato complexes could be found by comparing complexes **1–4**. Polymerizations of ethylene with trichlorobis[2-(benzylamido)pyridine]tantalum(V) and trichlorobis[2-(benzylamido)-4-methylpyridine]tantalum(V) (Fig. 1) should establish whether the electron-donating substituents increasing the activity. Comparisons are possible because the electron-donating methyl substituent is in the 4-position of the pyridine ring and therefore has only electronic effects. Similarly, trichlorobis[2-(benzylamido)-4-pyridine]tantalum(V) and trichlorobis[2-(benzylamido)-6-methylpyridine]tantalum(V) (Fig. 2) should give information about steric effects, changing four-substitution to six-substitution should not have an effect on electron density in the aromatic ring. Methyl at the six-position in pyridine should change the active site of the catalysts and prevent the complex from deactivation via dimerization.

In the bis(aminopyridinato) complexes Nb and Ta exhibit seven coordination, and the coordination spheres are pseudo-pentagonal bipyramids.[7,8,10] Four nitrogen atoms and one chloro ligand form the pentagonal plane. We calculated least-squares mean planes through the atoms forming the Ta–N4–$Cl_{equatorial}$ planes in the known seven-coordinated bis(aminopyridinato)tantalum complexes. In 2-(phenylamino)pyridinato complexes of niobium and tantalum,[7] corresponding atoms fit well to the calculated plane: all distances from the least-squares plane are less than 0.10 Å, whereas in benzylaminopyridinato complexes marked distortion is found:

* Al/Zr 2000 mol/mol, MAO 10 wt% in toluene, 300 ml toluene, p(et) = 5.0 bar, T = 60 °C for [Ta(BzNPy)$_2$Cl$_3$] and 80 °C for [Ta(PhNPyNHPh)$_2$Cl$_3$]; see also Ref. 6.

Table 3. Atomic coordinates ($\times 10^4$) equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for [Ta(BzN6MePy)$_2$Cl$_3$].

Atom	$10^4x/a$	$10^4x/b$	$10^4x/c$	10^3U_{eq}[a]/Å^2
Ta	−1655(2)	3229(1)	891(1)	30(1)
Cl1	−3209(2)	2243(2)	−620(2)	42(1)
Cl2	−182(2)	3446(2)	−175(2)	39(1)
Cl3	−3440(2)	3058(2)	1765(2)	44(1)
N1	−1374(7)	1370(6)	941(5)	36(2)
C2	−100(9)	1644(7)	1444(6)	33(2)
C3	815(9)	830(8)	1609(7)	38(2)
C4	329(10)	−305(8)	1266(7)	42(2)
C5	−997(10)	−590(8)	795(7)	41(2)
C6	−1865(9)	260(8)	634(6)	37(2)
C6m	−3318(9)	−31(8)	156(8)	47(2)
N7	57(7)	2837(6)	1719(5)	34(2)
C8	1430(9)	3379(8)	2041(7)	37(2)
C9	2154(10)	3332(8)	3061(7)	41(2)
C10	1505(11)	3050(8)	3741(7)	47(2)
C11	2206(13)	3077(10)	4669(8)	60(3)
C12	3573(15)	3361(11)	4917(9)	73(4)
C13	4237(14)	3629(11)	4252(11)	75(4)
C14	3542(11)	3611(10)	3322(10)	60(3)
N15	−2545(7)	4860(6)	572(5)	35(2)
C16	−2022(9)	5504(8)	1516(7)	37(2)
C17	−2330(10)	6630(8)	1916(8)	45(2)
C18	−3146(10)	7124(8)	1274(8)	46(2)
C19	−3597(9)	6502(8)	297(8)	43(2)
C20	−3276(9)	5374(8)	−65(7)	36(2)
C20m	−3711(10)	4707(8)	−1130(7)	43(2)
N21	−1221(8)	4786(6)	1942(5)	36(2)
C22	−812(10)	5118(8)	3021(6)	39(2)
C23	408(9)	5964(8)	3447(7)	40(2)
C24	929(11)	6230(10)	4459(8)	53(3)
C25	2036(12)	6994(11)	4890(9)	65(3)
C26	2646(12)	7507(10)	4332(10)	64(3)
C27	2161(12)	7253(10)	3325(10)	61(3)
C28	1037(10)	6485(8)	2888(7)	45(2)
C31	4677(12)	9946(9)	6656(8)	54(3)
C32	4010(13)	10643(10)	6115(9)	62(3)
C33	2635(13)	10764(10)	6023(8)	59(3)
C34	1828(14)	10206(11)	6462(8)	62(3)
C35	2484(15)	9503(11)	6997(9)	66(3)
C36	3883(16)	9396(10)	7093(8)	70(4)
C37	6171(14)	9825(12)	6761(11)	80(4)
C38	336(16)	10349(15)	6382(11)	88(4)

[a] See Table 2.

Table 4. Selected bond lengths (in Å) and angles (in °) in [Ta(BzN4MePy)$_2$Cl$_3$].

Ta–N1	2.215(4)	Ta–Cl1	2.435(2)
Ta–N7	2.064(3)	Ta–Cl2	2.383(2)
N1–Ta–N7	61.11(14)	N1–Ta–Cl1	77.50(10)
N1–Ta–N1^i	155.0(2)	N1–Ta–Cl2	85·15(11)
N1–Ta–N7^i	143.51(14)	N1–Ta–Cl2^i	94.09(11)
N7–Ta–N7^i	84.3(2)	N7–Ta–Cl1	137.83(10)
Cl1–Ta–Cl2	88.23(2)	N7–Ta–Cl2	95.58(10)
Cl2–Ta–Cl2^i	176.46(5)	N7–Ta–Cl2^i	87.05(10)

Symmetry transformation used to generate equivalent atoms: $^i -x, y, -z+3/2$.

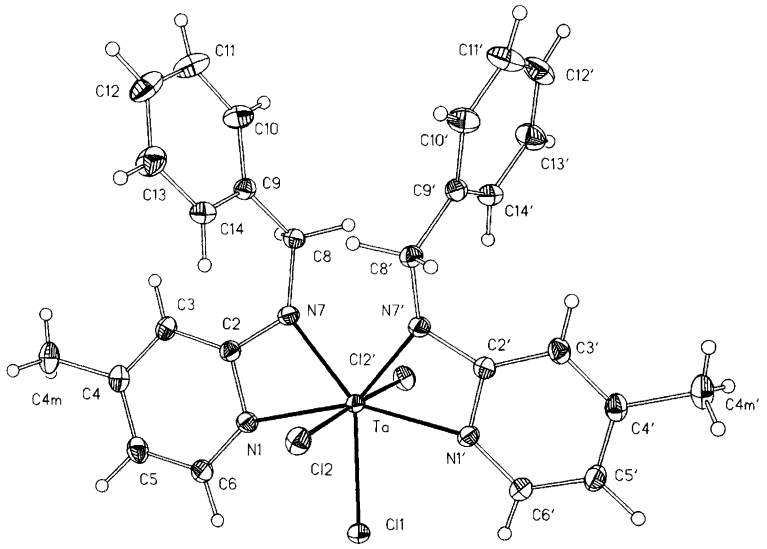

Fig. 1. Molecular structure of $[Ta(BzN4MePy)_2Cl_3]$ showing the labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 5. Selected bond lengths (in Å) and angles (in °) in $[Ta(BzN6MePy)_2Cl_3]$.

Ta–N1	2.289(7)	Ta–Cl1	2.418(3)
Ta–N7	2.044(7)	Ta–Cl2	2.377(3)
Ta–N15	2.300(7)	Ta–Cl3	2.410(3)
Ta–N21	2.038(7)		
N1–Ta–N7	60.1(3)	N1–Ta–Cl3	81.6(2)
N1–Ta–N15	163.1(2)	N7–Ta–Cl1	136.2(2)
N1–Ta–N21	132.8(3)	N7–Ta–Cl2	84.3(2)
N7–Ta–N15	136.7(3)	N7–Ta–Cl3	105.1(2)
N7–Ta–N21	81.2(3)	N15–Ta–Cl1	83.6(2)
N15–Ta–N21	60.2(3)	N15–Ta–Cl2	83.2(2)
Cl1–Ta–Cl2	85.27(10)	N15–Ta–Cl3	90.4(2)
Cl1–Ta–C13	87.18(10)	N21–Ta–Cl1	142.5(2)
Cl2–Ta–Cl3	170.58(8)	N21–Ta–Cl2	98.8(2)
N1–Ta–Cl1	81.1(2)	N21–Ta–Cl3	83.8(2)
N1–Ta–Cl2	102.7(2)		

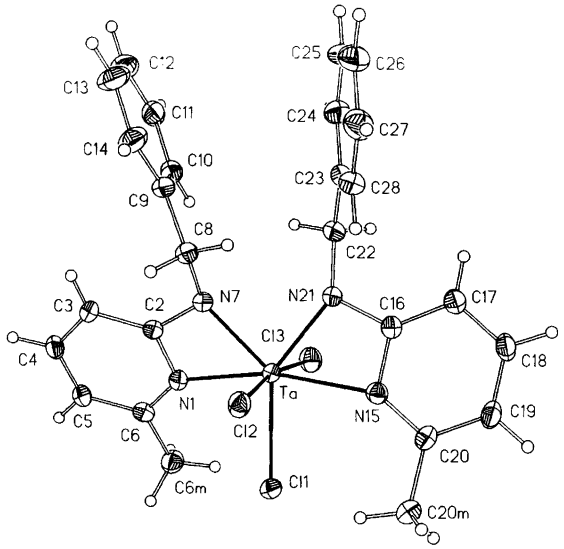

Fig. 2. Molecular structure of $[Ta(BzN6MePy)_2Cl_3]$ showing the labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. *p*-Xylene solvate molecule is omitted.

N atoms of the ligand lay ca. 0.20 Å away from the calculated plane.[8] Trichlorobis[2,6-di(phenylamino)-pyridinato]tantalum[9] is even more distorted, with a maximum deviation of 0.384(5) Å.

In the current complexes clear distortions can be observed: in $[Ta(BzN4MePy)_2Cl_3]$ atom distances from the calculated planes vary between 0.534(5) and 0.953(9) Å and in $[Ta(BzN6MePy)_2Cl_3]$ between 0.022(2) and 0.418(5) Å, respectively. Distortion does not have any clear effect on the Cl_{axial}–Ta–Cl_{axial} angles. In the most symmetrical complex, trichlorobis[2-(phenylamino)pyridinato]tantalum $[Ta(PhNPy)_2Cl_3]$,[7] the angle is 175.78(8)°, whereas in $[Ta(BzN4MePy)_2Cl_3]$ and $[Ta(BzN6MePy)_2Cl_3]$ these angles are 176.46(5) and 170.58(8)°, respectively. Distortion in these seven-coordinated complexes can be seen as a twist of the rigid aminopyridinato ligand: one nitrogen is located up from the plane, whereas the other nitrogen of the ligand is tilted downwards from the calculated least-squares mean plane. The other ligand is tilted similarly but to the opposite direction (Fig. 3). Typically N atoms have the longest distances from the least-squares mean planes (Table 6). Ta atoms are usually located very close to the calculated plane; distances are shorter than 0.02 Å, except in the highly distorted $[Ta(BzN4MePy)_2Cl_3]$, in which the distance 0.513(1) Å was calculated.

In **1** and **2** all Ta–Cl bond lengths are similar to those in previously reported tantalum aminopyridinato complexes. Typically a chloro ligand in the equatorial position has a slightly longer Ta–N bond than that occupying the axial position. Metal–nitrogen distances differ only slightly from the previously reported values for amino-pyridinato tantalum complexes. The Ta–N_{amino} and

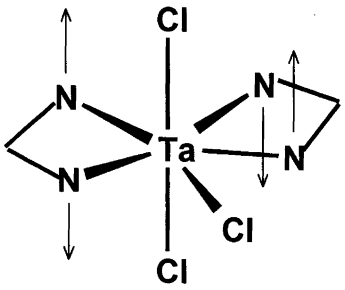

Fig. 3. Distortion in pseudo pentagonal bypyramidal coordination sphere of seven-coordinated aminopyrinato complexes.

Table 6. Average and maximum distortions of the pentagonal Ta–N_4–$Cl_{equatorial}$ plane in the seven-coordinated tantalum aminopyridinato complexes.

Complex	Average	Maximum deviation	Atom
[Ta(PhNPy)$_2$Cl$_3$][7]	0.057	0.089(2)	N_{amido}
[Ta(BzNPy)$_2$Cl$_3$][8]	0.143	0.225(5)	N_{amido}
[Ta(PhNPyNHPh)$_2$Cl$_3$][9]	0.245	0.384(5)	N_{amido}
[Ta(BzN4MePy)$_2$Cl$_3$]	0.779	0.953(9)	Cl
[Ta(BzN6MePy)$_2$Cl$_3$]	0.254	0.418(5)	N_{amido}

Ta–$N_{pyridinato}$ bonds are similar to those found previously, but in the case of [Ta(BzN6MePy)$_2$Cl$_3$][10] the Ta–$N_{pyridinato}$ distances are slightly longer (ca. 0.05 Å) than the average known values.

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