ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2018, Vol. 44, No. 2, pp. 162–168. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © M.V. Arsen'ev, L.S. Okhlopkova, A.I. Poddel'skii, G.K. Fukin, 2018, published in Koordinatsionnaya Khimiya, 2018, Vol. 44, No. 1, pp. 71–76.

Binuclear Triphenylantimony(V) Catecholate Based on Redox-Active Bis-*o*-Benzoquinone, a Bis-Catechol-Aldimine Derivative

M. V. Arsen'ev, L. S. Okhlopkova, A. I. Poddel'skii*, and G. K. Fukin

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhny Novgorod, 603950 Russia

**e-mail: aip@iomc.ras.ru*

Received July 7, 2017

Abstract—The oxidative addition of bis-*o*-benzoquinone Q–(CH=N–N=CH)–Q (L), in which two 3,5-di-*tert*-butyl-*o*-benzoquinones are linked to each other in positions 6 via the CH=N–N=CH group, to triphenylstibine gave a new binuclear triphenylantimony(V) bis-catecholate complex, Ph_3Sb(Cat–(CH=N–N=CH)–Cat)$SbPh_3$ (**I**). Recrystallization of **I** from a methanol–trichloromethane mixture resulted in an additional coordination of a methanol molecule to each antimony atom to give the binuclear complex, $(CH_3OH)Ph_3Sb$(Cat–(CH=N–N=CH)–Cat)$SbPh_3(CH_3OH)$ (**I** · $2CH_3OH$), the crystals of which (**I** · $2CH_3OH$) · $2CH_3OH$ · $CHCl_3$ (**II**) contain additionally two methanol solvate molecules, which fix the geometry of the nitrogen-containing bridging group, and a trichloromethane molecule. The molecular structure of compound **II** in the crystalline state was determined by X-ray diffraction (CIF file CCDC no. 1560840).

Keywords: redox active, antimony, bis-*o*-benzoquinone, catecholate, X-ray diffraction

DOI: 10.1134/S1070328418020021

INTRODUCTION

The coordination chemistry of redox-active *o*-quinone type ligands has considerably progressed in recent years. *o*-Quinone complexes have been obtained for virtually all transition metals [1–4] and main group metals [5–7]. The interest in the *o*-quinone and related metal complexes is largely associated with the presence of several redox states of such ligands. As a result, their complexes show a diversity of structural types, serve as promising objects for studying magnetochemical properties, including magnetic exchange interactions, between the paramagnetic metal and paramagnetic ligand forms, and possess interesting redox properties [1, 8–11]. The main group metal complexes with *o*-quinone ligands are able to undergo various types of reactions impossible for the "classic" main group metal complexes such as the oxidative addition and reductive elimination characteristic of transition metal compounds. An example of such reactions is reversible addition of the molecular oxygen, first described for main group (antimony) metal complexes in 2005 [12].

Linking two redox-active *o*-quinone centers by bridging groups gives rise to various bis-*o*-quinones, whose coordination chemistry has also markedly progressed [13–18]. Bis-*o*-benzoquinone (L) with the azine bridging group, a 6-formyl-3,5-di-*tert*-butyl-*o*-benzoquinone derivative, has been described in [19]. Here we report a binuclear triphenylantimony(V) complex based on this ligand L.

EXPERIMENTAL

Experiments on the synthesis of complexes were carried out in evacuated tubes in the absence of oxygen. The solvents used in the study were purified and dehydrated by standard procedures [20]. The ligand L was prepared by the procedure described in [19].

The ^1H NMR spectra were recorded on a Bruker AVANCE DPX-200 spectrometer using tetramethylsilane as the internal standard and $CDCl_3$ as the solvent. IR spectrum was measured on a FTIR spectrometer (on KBr glasses, in mineral oil).

Synthesis of Ph_3Sb(Cat–(CH=N–N=CH)–Cat)$SbPh_3$ (I). Weighed portions of L (0.246 g, 0.5 mmol) and $SbPh_3$ (0.353 g, 1 mmol) were dissolved in degassed THF with vigorous stirring. Upon dissolution, the *o*-quinone color gradually disappeared and the solution became yellow-orange. The solvent was removed and the product was recrystal-

Table 1. Crystallographic data and X-ray experiment and structure refinement details for compound **II**

Parameter	Value
M	1446.28
T, K	100(2)
System	Triclinic
Space group	$P\bar{1}$
Unit cell parameters:	
a, Å	13.9004(3)
b, Å	14.3729(3)
c, Å	18.4021(3)
α, deg	78.8857(16)
β, deg	85.6254(15)
γ, deg	72.663(2)
V, Å^3	3442.98(12)
Z	2
ρ(calcd.), g/cm^3	1.395
μ, mm^{-1}	0.955
F(000)	1488
$2\theta_{max}$, deg	56
Number of measured reflections	64340
Number of unique reflections	16543
R_{int}	0.0519
Number of refined parameters	816
R_1, wR_2 ($I > 2\sigma(I)$)	0.0367, 0.0746
R_1, wR_2 (all data)	0.0542, 0.0791
GOOF on F^2	1.046
Residual electron density (max/min), e/Å^3	0.937/–0.823

lized from *n*-hexane. Complex **I** was isolated as a pale yellow amorphous powder. The yield was 0.44 g (73%).

For $C_{66}H_{70}N_2O_4Sb_2$

Anal. calcd., %	C, 66.13	H, 5.89	Sb, 20.31
Found, %	C, 66.40	H, 5.97	Sb, 20.55

IR (ν, cm^{-1}): 693, 730, 1245, 1260, 1588, 1632. ^{1}H NMR ($CDCl_3$; δ, ppm): 1.41 (s, 18 H, 2^{t}Bu), 1.48 (s, 18 H, 2^{t}Bu), 6.82 (s, 2H, $2C_6H_{1\ Ar}$), 7.2–7.6 (m, 18 H, Ph), 7.7–7.9 (m, 12H, Ph), 9.44 (s, 2H, 2 CH=N).

Recrystallization of product **I** (0.3 g) from 20 mL of a methanol–trichloromethane mixture (1 : 1) gave almost colorless crystals of $(CH_3OH)Ph_3Sb(Cat–(CH=N–N=CH)–Cat)SbPh_3(CH_3OH) \cdot 2CH_3OH \cdot CHCl_3$ (**I** $\cdot 2CH_3OH$) $\cdot 2CH_3OH \cdot CHCl_3$ (**II**). The yield was 0.23 g (63.5%).

For $C_{71}H_{87}N_2O_8Cl_3Sb_2$

Anal. calcd., %	C, 58.96	H, 6.06	Sb, 16.84
Found, %	C, 59.15	H, 6.14	Sb, 16.62

IR (ν, cm^{-1}): 695, 735, 1242, 1260, 1588, 1628, 3220. ^{1}H NMR (DMSO-d^6; 400 MHz; δ, ppm): 1.40 (s, 36H, ^{t}Bu), 3.16 (d, 5 Hz, 12H, CH_3, CH_3OH), 4.10 (q, 5 Hz, 4H, OH, CH_3OH), 6.70 (s, 2H, $C_6H_{1\ Ar}$), 7.30–7.36 (m, 18H, Ph), 7.65–7.70 (m, 12H, Ph), 8.32 (s, 1H, $CHCl_3$), 9.15 (s, 2H, CH=N).

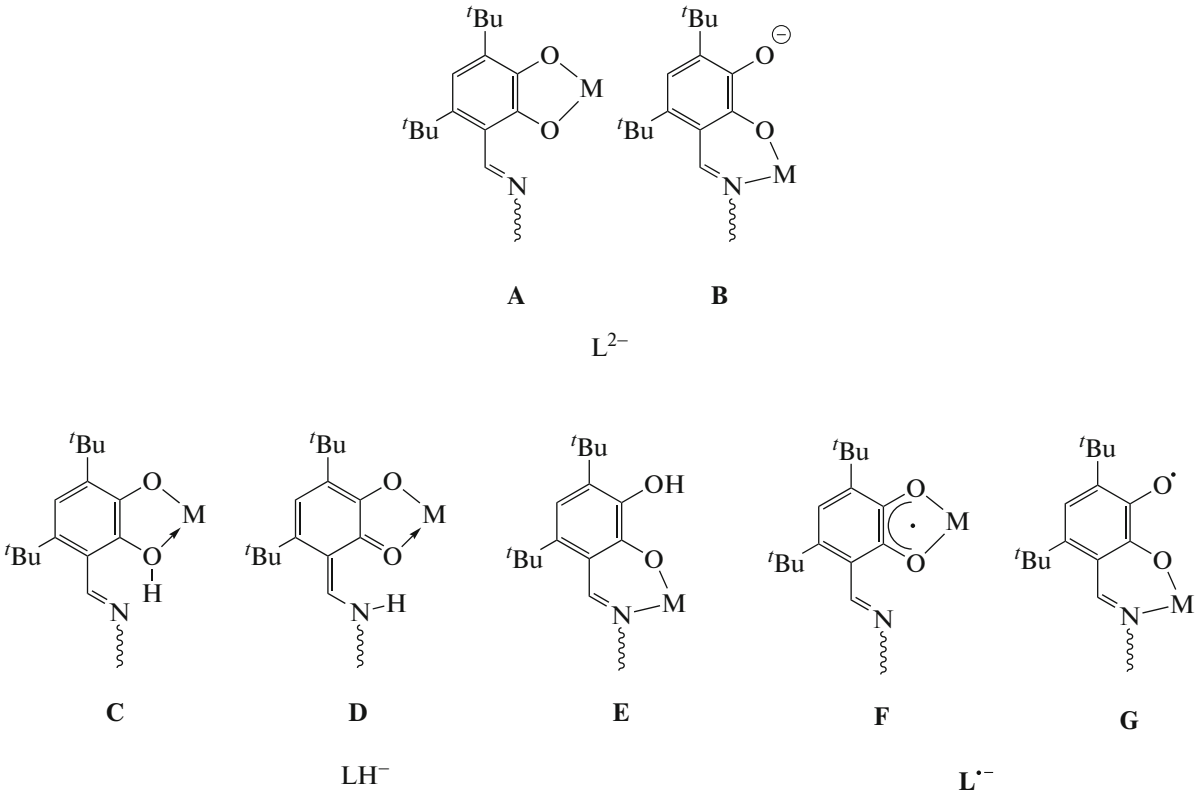
The crystals suitable for X-ray diffraction were grown from a $CHCl_3$–MeOH solvent mixture.

The X-ray diffraction study of **II** was carried out on a Xcalibur diffractometer at 100 K. The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2_{hkl} in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were placed into the geometrically calculated positions and refined isotropically. The calculations were carried out by the SHELXTL program package [21]. The absorption corrections were applied by the SCALE3 ABSPACK program package [22]. The crystal data and X-ray experiment and structure refinement details for compound **II** are summarized in Table 1.

The crystal structure data for compound **II** were deposited with the Cambridge Crystallographic Data Centre (no. 1560840; deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

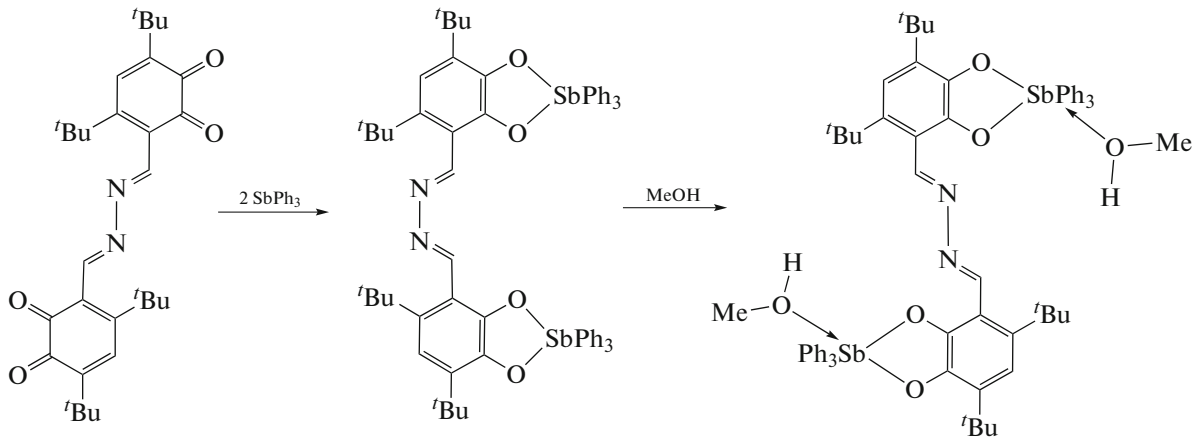
Catechols (catecholates) are prone to O,O'-coordination when complexed with metals. The presence of an additional coordination site in catechol-aldimines, that is, the nitrogen atom of the aldimine moiety, considerably increases the number of possible structures that are formed upon chelation of one metal center. In this case, both the O,O'-coordination by the catecholate moiety and the O,N-coordination by the salicylaldimine moiety are possible. For the dianionic (doubly deprotonated) form of catechol-aldimines, two isomers can form (**A** and **B**, Scheme 1), while for monodeprotonated catechol-aldimines, three isomers (**C**–**E**) are possible. The *o*-semiquinone form of the ligand can also give rise to two isomers (**F** and **G**, Scheme 1). This can considerably hamper identification of the resulting metal complexes, but also opens up opportunities for the preparation of polymetallic and polynuclear metal complexes. In addition, the azine group present in L (Scheme 2) can make the structure more sophisticated by additional intermolecular contacts with neighboring molecules and solvent molecules.



Scheme 1

Bis-*o*-benzoquinone (**L**) reacts with triphenylstibine in 1 : 2 molar ratio in a toluene solution to give triphenylantimony(V) bis-catecholate **I** (Scheme 2). Complex **I** isolated from hexane is a pale yellow amorphous powder. According to ^{1}H NMR spectroscopy, the catecholate moieties $CatSbPh_3$ are equivalent in solution.

The recrystallization of complex **I** from a methanol–trichloromethane mixture (1 : 1) affords almost colorless crystals of compound **II**, which contains two methanol molecules coordinated to antimony atoms, two methanol solvation molecules, and a trichloromethane molecule.



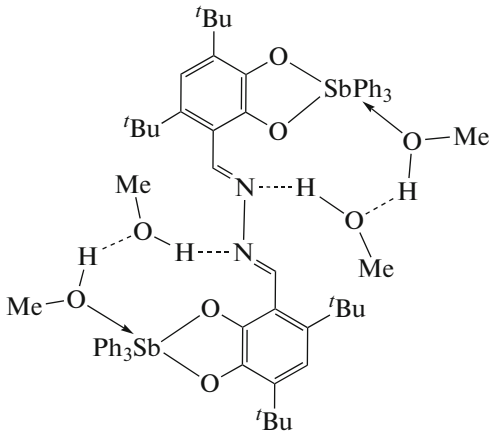
Q–(CH=N–N=CH)–Q

L

Ph_3Sb(Cat–(CH=N–N=CH)–Cat)$SbPh_3$

I

I · $2CH_3OH$



(CH_3OH)Ph_3Sb(Cat–(CH=N–N=CH)–Cat)$SbPh_3$(CH_3OH) · $2CH_3OH$

(**I** · $2CH_3OH$) · $2CH_3OH$

Scheme 2

In the crystal of **II**, both antimony atoms, Sb(1) and Sb(2), occur in octahedral environments formed by three phenyl groups, oxygen atoms of the chelating ligands, and methanol molecules (Fig. 1). The Sb(1) and Sb(2) atoms are located on one side of the C(33)N(1)N(2)C(34) bridge. The Sb(1)···Sb(2) distance (8.547(2) Å) is comparable with the Ti···Ti distances between the titanium atoms (8.70 Å) in the helicate complexes of non-shielded bis-catechol of a similar structure [23].

The Sb(1)O(1)C(1)C(2)O(2) and Sb(2)O(3)C(36)C(37)O(4) metallacycles are nearly planar. The O(1)C(1)C(2)O(2) and O(3)C(36)C(37)O(4) torsion angles are 0.91(6)° and 2.66(6)°, respectively. The folding angles at the O(1)···O(2) and O(3)···O(4) lines in the chelate rings are 2.84(6)° and 5.53(6)°, respectively. The Sb(1)–O(1), Sb(1)–O(2), Sb(2)–O(3), and Sb(2)–O(4) distances (Table 2) are somewhat shorter than the sum of covalent radii of antimony and oxygen (1.43 Å + 0.73 Å = 2.16 Å [24]) and are in line with the bond lengths in various triarylantimony(V) catecholates [25–29]. The geometric characteristics (C–O distances in the O,O'-chelating moieties at each antimony atom and the C–C distances in the C_6 rings) are indicative of the dianionic (catecholate) form of coordination [30–34]. Each moiety is the triphenylantimony(V) catecholate complex with a coordinated methanol molecule.

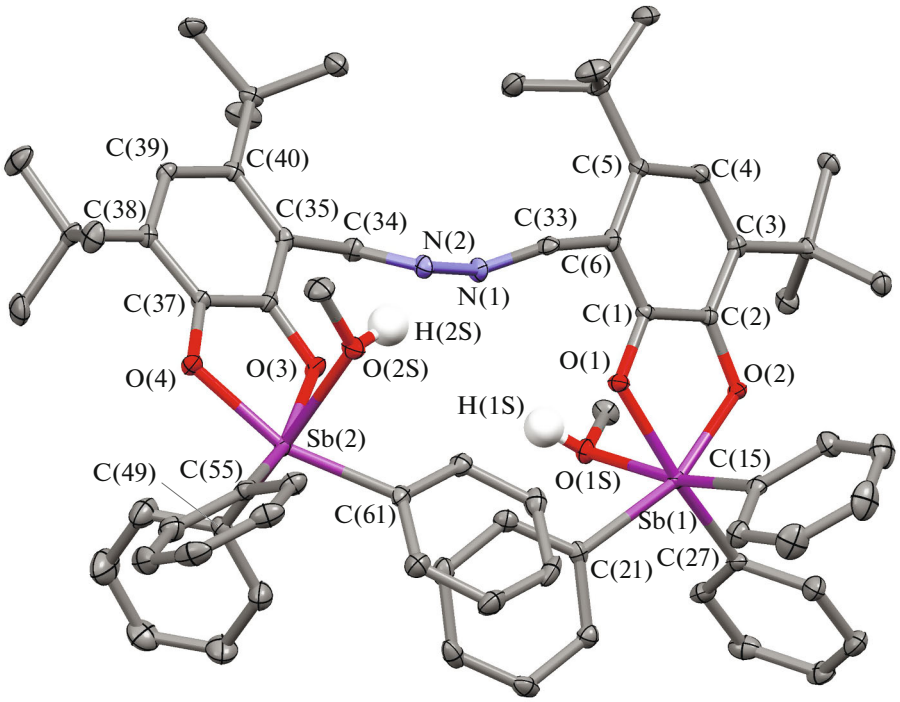


Fig. 1. Molecular structure of complex **I** · $2CH_3OH$ in the crystals of **II**. The hydrogen atoms (except for the hydroxyl hydrogens of the coordinated methanol molecules) and methanol and trichloromethane solvate molecules are omitted. The ellipsoids are given at a 50% probability.

In the unit cell of **II**, two methanol molecules are additionally coordinated via hydrogen bonds between the hydroxyl groups and the nitrogen atom of the bridge (Fig. 2). In the O(1S)–H(1S)···O(3S) and O(2S)–H(2S)···O(4S) contacts, the H···O distances are 1.84(2) and 1.82 Å (the corresponding O(1S)H(1S)O(3S) and O(2S)H(2S)O(4S) angles are 170° and 173°). The O···N contacts in the O(3S)–H(3S)···N(1) and O(4S)–H(4S)···N(2) hydrogen bonds are 2.05 and 2.02 Å (the corresponding O(3S)H(3S)N(1) and O(4S)H(4S)N(2) angles are 175° and 172°) (Fig. 2a). Unlike neutral L and the corresponding bis-catechol [19], the C(33)N(1)-N(2)C(34) moiety is distorted, with the C(33)N(1)N(2)C(34) dihedral angle being 145.8(1)°, and the aldimine C(33) and C(34) atoms deviate from the plane of the catecholate moieties by less than 0.12 Å. The angle between the catecholate planes is 22.0° (Fig. 2b). The two additional methanol molecules are held by hydrogen bonds, so that the geometry

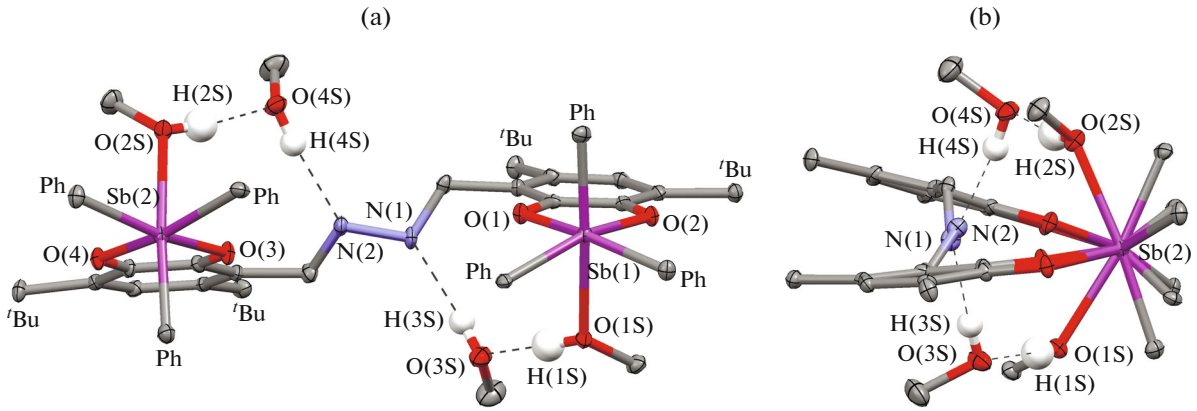


Fig. 2. (a) Fragment of the molecule (**I** · $2CH_3OH$) · $2CH_3OH$ with indicated hydrogen bonds with methanol molecules (the carbon atoms of the phenyl and *tert*-butyl groups are omitted); (b) view of the molecule of (**I** · $2CH_3OH$) · $2CH_3OH$ along the line connecting the antimony atoms Sb(1) and Sb(2).

Table 2. Selected bond lengths and bond angles in compound **II**

Bond	*d*, Å
Sb(1)–O(1)	2.0444(12)
Sb(1)–O(2)	2.0335(11)
Sb(2)–O(3)	2.0482(11)
Sb(2)–O(4)	2.0478(11)
Sb(1)–O(1S)	2.3866(11)
Sb(2)–O(2S)	2.3743(14)
Sb(1)–C(15)	2.1331(17)
Sb(1)–C(21)	2.1428(17)
Sb(1)–C(27)	2.1525(18)
Sb(2)–C(49)	2.1421(19)
Sb(2)–C(55)	2.1472(18)
Sb(2)–C(61)	2.1347(16)
O(1)–C(1)	1.358(2)
O(2)–C(2)	1.362(2)
O(3)–C(36)	1.352(2)
O(4)–C(37)	1.362(2)
N(1)–C(33)	1.272(2)
N(2)–C(34)	1.274(2)
N(1)–N(2)	1.427(2)
Angle	**ω, deg**
O(2)Sb(1)O(1)	80.49(5)
O(2)Sb(1)C(21)	158.88(5)
O(1)Sb(1)C(27)	164.00(5)
C(15)Sb(1)O(1S)	171.12(6)
O(4)Sb(2)O(3)	79.34(5)
O(3)Sb(2)C(55)	160.02(6)
O(4)Sb(2)C(61)	161.13(6)
C(49)Sb(2)O(2S)	174.02(5)

of the bridging group in the redox-active ligand can be regarded as fixed (Fig. 2).

Thus, a new binuclear triphenylantimony(V) bis-catecholate complex was synthesized from bis-*o*-benzoquinone containing a CH=N–N=CH bridging group. The molecular structure of the complex isolated from a methanol–trichloromethane mixture as $(CH_3OH)Ph_3Sb(Cat–(CH=N–N=CH)–Cat)SbPh_3(CH_3OH) \cdot 2CH_3OH \cdot CHCl_3$ (**II**) was established by X-ray diffraction. It was found that the presence of methanol molecules, both antimony coordinated and occurring as solvate molecules, gives rise to intermolecular hydrogen bonds with the nitrogen atoms of the bis-catecholate bridging group, thus fixing the geometry of the CH=N–N=CH bridge and the bis-catecholate complex as a whole.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 16-33-60157 mol_a_dk).

REFERENCES

1. Pierpont, C.G., *Coord. Chem. Rev.*, 2001, vols. 219–221, p. 415.
2. Pierpont, C.G. and Buchanan, R.M., *Coord. Chem. Rev.*, 1981, vol. 38, no. 1, p. 45.
3. Zanello, P. and Corsini, M., *Coord. Chem. Rev.*, 2006, vol. 250, p. 2000.
4. Kharisov, B.I., Méndez-Rojas, M.A., Garnovskii, A.D., et al., *J. Coord. Chem.*, 2002, vol. 55, no. 7, p. 745.
5. Kabachnik, M.I., Bubnov, N.N., Prokof'ev, A.I., and Solodovnikov, S.P., *Sci. Rev.*, 1981, vol. 24, p. 197.
6. Piskunov, A.V. and Poddel'sky, A.I., *Glob. J. Inorg. Chem.*, 2011, vol. 2, no. 2, p. 110.
7. Baryshnikova, S.V., Bellan, E.V., Poddel'sky, A.I., et al., *Eur. J. Inorg. Chem.*, 2016, p. 5230.
8. Pierpont, C.G., *Coord. Chem. Rev.*, 2001, vols. 216–217, p. 99.
9. Sato, O., Tao, J., and Zhang, Yu.-Zh., *Angew. Chem., Int. Ed. Engl.*, 2007, vol. 46, p. 2152.
10. Kaim, W., *Inorg. Chem.*, 2011, vol. 50, p. 9752.
11. Bubnov, M.P., Skorodumova, N.A., Arapova, A.V., et al., *Inorg. Chem.*, 2015, vol. 54, no. 16, p. 7767.
12. Abakumov, G.A., Poddel'sky, A.I., Grunova, E.V., et al., *Angew. Chem., Int. Ed. Engl.*, 2005, vol. 44, p. 2767.
13. Abakumov, G.A., Nevodchikov, V.I., Druzhkov, N.O., et al., *Izv. Akad. Nauk, Ser. Khim.*, 1997, vol. 46, p. 804.
14. Abakumov, G.A., Cherkasov, V.K., Nevodchikov, V.I., et al., *Inorg. Chem.*, 2001, vol. 40, p. 2434.
15. Shultz, D.A., *Comments Inorg. Chem.,* 2002, vol. 23, p. 1.
16. Caneschi, A., Dei, A., Mussari, C.P., et al., *Inorg. Chem.*, 2002, vol. 41, p. 1086.
17. Piskunov, A.V., Cherkasov, V.K., Druzhkov, N.O., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2005, vol. 54, p. 1580.
18. Poddel'sky, A.I., Piskunov, A.V., Druzhkov, N.O., et al., *Z. Anorg. Allg. Chem.*, 2009, vol. 635, p. 2563.
19. Arsenyev, M.V., Baranov, E.V., Fedorov, A.Yu., et al., *Mendeleev Commun.*, 2015, vol. 25, p. 312.
20. Gordon, A. and Ford, R., *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.
21. Sheldrick, G.M., *SHELXTL. Version 6.14. Structure Determination Software Suite*, Madison: Bruker AXS, 2003.
22. *SCALE3 ABSPACK: Empirical Absorption Correction, CrysAlis Pro—Software Package*, Agilent Technologies, 2012.
23. Albrecht, M., Kamptmann, S., and Frohlich, R., *Polyhedron*, 2003, vol. 22, p. 643.

24. Batsanov, S.S., *Zh. Neorg. Khim.*, 1991. vol. 36. no. 12, p. 3015.
25. Fukin, G.K., Zakharov, L.N., Domrachev, G.A., et al., *Izv. Akad. Nauk., Ser. Khim.*, 1999, p. 1744.
26. Poddel'sky, A.I., Smolyaninov, I.V., Somov, N.V., et al., *J. Organomet. Chem.*, 2010, vol. 695, no. 4, p. 530.
27. Poddel'sky, A.I., Smolyaninov, I.V., Kurskii, Yu.A., et al., *J. Organomet. Chem.*, 2010, vol. 695, no. 8, p. 1215.
28. Poddel'sky, A.I., Baranov, E.V., Fukin, G.K., et al., *J. Organomet. Chem.*, 2013, vol. 733, p. 44.
29. Poddel'skii A.I., Ilyakina E.V., Smolyaninov I.V., et al., *Izv. Akad. Nauk., Ser. Khim.*, 2014, no. 4, p. 923.
30. Poddel'sky, A.I., Smolyaninov, I.V., Berberova, N.T., et al., *J. Organomet. Chem.*, 2015, vols. 789–790, p. 8.
31. Poddel'sky, A.I., Smolyaninov, I.V., Fukin, G.K., et al., *J. Organomet. Chem.*, 2016, vol. 824, p. 1.
32. Tofan, D. and Gabbai, F.P., *Chem. Sci.*, 2016, vol. 7, p. 6768.
33. Poddel'sky, A.I., Druzhkov, N.O., Fukin, G.K., et al., *Polyhedron*, 2017, vol. 124, p. 41.
34. Poddel'sky, A.I., Arsenyev, M.V., Astaf'eva, T.V., et al., *J. Organomet. Chem.*, 2017, vol. 835, p. 17.

Translated by Z. Svitanko