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A New Approach to the Synthesis of Gallium(III) Complexes with α-Diimine Ligands in the Radical Anion Form

P. A. Petrov[a, b, *], **S. N. Konchenko**[a, b], **and V. A. Nadolinny**[a]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences,*
pr. akademika Lavrent'eva 3, Novosibirsk, 630090 Russia
[b] *Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia*
**e-mail: panah@niic.nsc.ru*

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Abstract—A convenient method for the synthesis of gallium(III) complexes with α-diimine ligands $DAB^{Me,Mes}$ (*N*,*N*'-(butane-2,3-diylidene)bis(2,4,6-trimethylaniline)) or $BIAN^{Dipp}$ (1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) in the radical anion form is found. The method includes the reaction of complexes $[Co(DAB^{Me,Mes})Cl_2]$ and $[Co(BIAN^{Dipp})Cl_2]$ with gallium resulting in the transmetallation and one-electron reduction of the ligand. The synthesized complexes $[Ga(DAB^{Me,Mes})Cl_2]$ and $[Ga(BIAN^{Dipp})Cl_2]$ are characterized by X-ray diffraction analysis and EPR spectroscopy.

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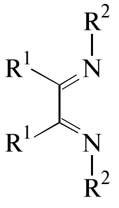
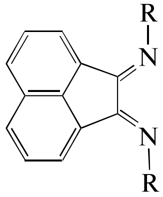
INTRODUCTION

Interest in metal complexes with α-diimines, namely, diazabutadienes (DAB^{R^1,R^2}) and acenaphthenediimines ($BIAN^R$),



DAB^{R^1,R^2}



$BIAN^R$

is mainly caused by their catalytic activity in α-olefin polymerization [1, 2] and several other reactions [3–5]. Diversity of coordination modes of α-diimines [6–12] and their ability to undergo reversible stepwise reduction to the radical anion and dianion make it possible to stabilize unusual element–element bonds and low oxidation states of the metal atoms [13, 14]. Examples for this stabilization are the anionic gallium(I) complexes $[(L^{NN})Ga]^-$ (L^{NN} = α-diimine ligand) being analogs of heterocyclic carbenes. This makes it possible to use these complexes as ligands towards a series of transition and nontransition metals and to synthesize compounds with the gallium–metal bond [15–20]. The halide (predominantly iodide) complexes $[Ga(L^{NN})Hal_2]$ or dimers $[(L^{NN})Ga–Ga(L^{NN})]$ are common precursors of the anionic complexes $[(L^{NN})Ga]^-$.

The present work is devoted to the development of a convenient synthetic approach to complexes $[Ga(L^{NN})X_2]$. The transmetallation reaction, viz., the interaction of $[Co(L^{NN})Cl_2]$ with metallic gallium, is proposed as this approach.

EXPERIMENTAL

The complexes were synthesized under argon using the standard Schlenk technique. The solvents for the syntheses were dehydrated and degassed by reflux and distillation under inert gas using the corresponding drying agents [21]. The starting complexes $[Co(DAB^{Me,Mes})Cl_2]$ [22] and $[Co(BIAN^{Dipp})Cl_2]$ [23] were synthesized using published procedures. IR spectra in KBr pellets were recorded on a SCIMITAR FTS 2000 instrument. EPR spectra in the X range of frequencies were detected at 298 K on a Varian E-109 instrument using diphenylpicrylhydrazyl ($g = 2.0036$) as a standard for the determination of the g factor. The EPR spectra were simulated using the Simfoniya program.

Synthesis of $[Ga(DAB^{Me,Mes})Cl_2]$ (I). Solid $[Co(DAB^{Me,Mes})Cl_2]$ (330 mg, 0.733 mmol) and Ga (215 mg, 3.08 mmol) were placed in a Schlenk flask, and tetrahydrofuran (THF) (25 mL) was condensed into it. The flask was evacuated to a residual pressure of ~0.1 mm Hg, hermetically closed, and let to warm to room temperature, after which the flask was heated at the temperature of the bath (55°C) with vigorous stirring for 2 days. A black residue was filtered using a glass frit (G4), the solution was evaporated, and the residue was extracted with diethyl ether (30 mL). The solution was filtered and kept at –24°C for 24 h. Red crystals suitable for X-ray diffraction analysis were dried in vacuo. The yield was 115 mg (35%).

Table 1. Crystallographic data and refinement parameters for structures **I** and **II** $\cdot$ 0.5Et_2O

Parameter	Value	
	I	**II** $\cdot$ 0.5Et_2O
Molecular weight	461.08	678.38
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
Temperature, K	200	150
a, Å	8.1890(16)	12.036(2)
b, Å	18.191(4)	14.971(3)
c, Å	15.482(3)	19.956(4)
α, deg	90	88.96(3)
β, deg	102.93(3)	83.22(3)
γ, deg	90	82.17(3)
V, Å^3	2247.8(8)	3537.5(12)
Z	4	4
$F(000)$	956	1424
μ, mm^{-1}	1.471	0.958
Crystal size, mm	0.18 × 0.14 × 0.10	0.08 × 0.06 × 0.04
θ Range of data collection, deg	1.75–26.73	1.71–29.24
Index range h, k, l	$-10 \le h \le 9, -23 \le k \le 22, -19 \le l \le 19$	$-14 \le h \le 16, -20 \le k \le 20, -27 \le l \le 27$
T_{min}, T_{max}	0.826, 0.893	0.789, 0.894
Number of measured/independent/observed ($I > 2\sigma(I)$) reflections	19788/4757/4190	37045/18523/10585
R_{int}	0.0503	0.1153
R_1, wR_2 ($I > 2\sigma(I)$)	0.0307, 0.0815	0.0640, 0.1185
R_1, wR_2 (all reflections)	0.0360, 0.0838	0.1431, 0.1679
Goodness-of-fit	1.053	0.895
Number of refined parameters	252	802
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.42/–0.39	1.11/–1.69

IR spectrum (KBr), ν, cm^{-1}: 1638 w, 1605 w, 1572 m, 1476 s, 1439 s, 1400 s, 1304 w, 1250 s, 1220 m, 1121 m, 986 m, 886 m, 856 m, 571 m, 549 m, 412 m.

For $C_{22}H_{28}N_2Cl_2Ga$

anal. calcd., %:	C, 57.31;	H, 6.12;	N, 6.07.
Found, %:	C, 57.73;	H, 6.12;	N, 5.93.

Synthesis of [Ga(BIAN^{Dipp})Cl_2] (II) was carried out similarly by heating [Co(BIAN^{Dipp})Cl_2] (258 mg, 0.409 mmol) and Ga (210 mg, 3.01 mmol) in THF (30 mL) for 14 days. Dark violet crystals were dried in vacuo. The yield was 130 mg (50%).

IR spectrum (KBr), ν, cm^{-1}: 1593 m, 1538 s, 1466 s, 1384 m, 1363 m, 1321 s, 1255 m, 1215 m, 1188 m, 1147 m, 1057 m, 935 m, 897 m, 823 m, 804 m, 764 s, 671 m, 595 w, 548 w, 459 m, 417 m.

For $C_{36}H_{40}N_2Cl_2Ga$

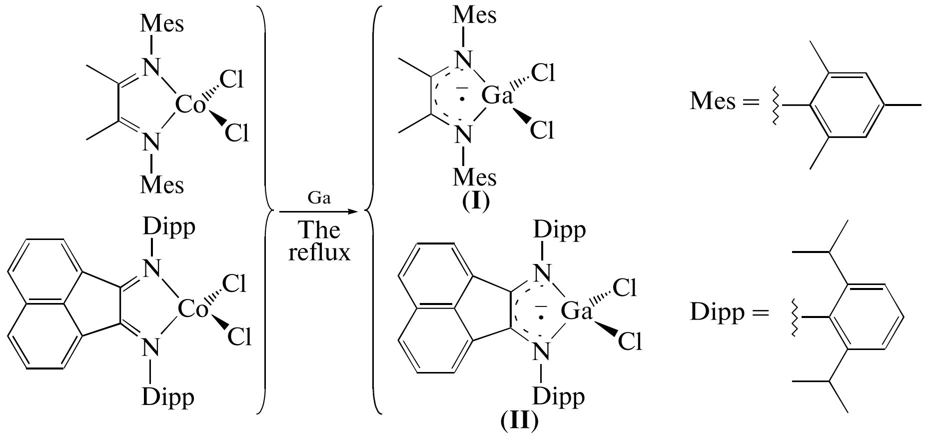
anal. calcd., %:	C, 67.42;	H, 6.29;	N, 4.37.
Found, %:	C, 67.50;	H, 6.51;	N, 3.97.

X-ray diffraction analysis. Crystallographic and X-ray diffraction data for the determination of structures **I** and **II** $\cdot$ 0.5Et_2O were obtained on a Bruker X8 Apex CCD automated diffractometer (graphite monochromator, MoK_α radiation, $\lambda = 0.71073$ Å). An absorption correction was applied semiempirically (SADABS) [24]. The structure was solved by a direct method and refined by least squares in the anisotropic approximation (SHELXTL) [25]. Hydrogen atoms were geometrically localized and refined in the rigid body approximation. The most important crystallographic data and refinement parameters for the structures are presented in Table 1. Selected bond lengths and angles are given in Table 2.

The coordinates of non-hydrogen atoms were deposited with the Cambridge Crystallographic Data Centre (CCDC 1001321 (**I**) and 1001322 (**II** · $0.5Et_2O$); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) and are available from the authors.

RESULTS AND DISCUSSION

The interaction of cobalt complex $[Co(DAB^{Me,Mes})Cl_2]$ with an excess of elementary Ga in THF at 50°C leads to the fast transformation of the initial green suspension into an orange-red solution with a black precipitate. Red crystals of compound **I** were obtained by the evaporation of the solution and the recrystallization of the residue from diethyl ether. In the course of the reaction Ga(0) is oxidized to Ga(III), whereas neutral ligand DAB is reduced to the radical anion form



The black powder formed as a by-product presumably contains metallic cobalt; however, no satisfactory powder diffraction data were obtained. Complex **II** was synthesized similarly but within a substantially longer time.

The above mentioned diversity of the coordination mode of the diazabutadiene ligands (especially with aliphatic substituents at the nitrogen atoms) and their oxidation state leads to many stoichiometric ratios of complexes in the gallium–diazabutadiene–halogen system. The mononuclear iodide analogs of complexes **I** and **II** have been synthesized earlier by the reaction of 'GaI' and neutral diazabutadiene [26–29]. Complex $[Ga(DAB^{Me,Dipp})Cl_2]$ (**III**) was synthesized from $GaCl_3$ and generated in situ salt $Na(DAB^{Me,Dipp})$ [19]. The reaction of lithium salt $Li_2(DAB^{H,R})$ (R is *tert*-Bu, cyclohexyl) and $GaCl_3$ affords binuclear gallium(III) complexes $[Ga(DAB^{H,R})Cl]_2$ of two types in each of which the dianionic form of DAB is coordinated to the Ga atoms via the bidentate-bridging mode [30, 31]. The reaction of $K(Tmeda)[Ga^I(DAB^{H,Dipp})]$ with complex $[Mo(CO)_2(PPh_3)_2Br_2]$ gives dimer $[Ga^{II}(DAB^{H,Dipp})Br]_2$ instead of the expected formation of the Mo–Ga bond [32]. Its iodide analog $[Ga^{II}(DAB^{H,Dipp})I]_2$ is formed (along with $[Ga^{III}(DAB^{H,Dipp})_2]$) by the reaction of $K(Tmeda)[Ga^I(DAB^{H,Dipp})]$ and 'GaI' [32]. Cationic gallium(III) complexes with neutral diazabutadiene ligands $[Ga(L^{NN})Cl_2][GaCl_4]$ are formed by the reac-

Table 2. Parameters of coordination nodes and chelates in molecules **I** and **II**

	I	II	
	Bond, Å		
Ga–Cl	2.1712(7)	2.1482(13)	2.1515(13)
	2.1467(8)	2.1590(12)	2.1530(13)
Ga–N	1.9264(16)	1.946(3)	1.947(3)
	1.9208(15)	1.940(3)	1.956(3)
C–N	1.343(2)	1.332(5)	1.331(4)
	1.355(2)	1.336(5)	1.336(4)
C–C	1.427(3)	1.444(5)	1.429(5)
	Angle, deg		
Cl–Ga–Cl	108.00(3)	110.73(6)	111.03(5)
N–Ga–N	86.33(6)	87.26(13)	87.32(13)

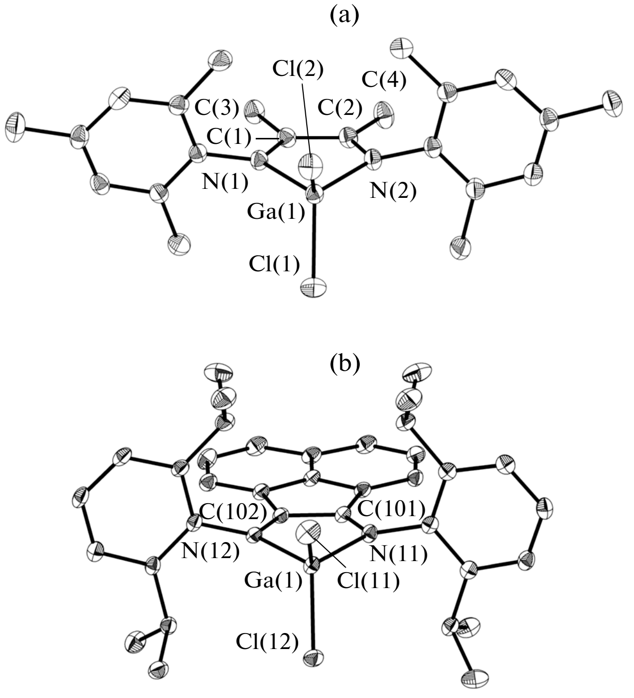


Fig. 1. Molecular structures of complexes (a) **I** and (b) **II**. Hydrogen atoms are omitted. One of the crystallographically independent molecules is presented for structure **II**.

tions of L$^{\text{NN}}$ (DAB$^{\text{H},t\text{Bu}}$ or BIAN$^{\text{Dipp}}$) with GaCl$_3$ [33, 34]. Advantages of the proposed method for the synthesis of the gallium complexes with diazobutadienes in the radical anion form are the use of the initial substances resistant to oxygen and moisture and no necessity in additional reducing agents, such as alkaline metals.

The reflux of complex [Co(DAB$^{\text{Me,Dipp}}$)Cl$_2$] with a gallium excess for 2 weeks gave a light orange solution from which neither compound **III**, nor other individual products were isolated. The interaction of [Zn(DAB$^{\text{Me,Dipp}}$)Cl$_2$] with Ga under the conditions of formation of compound **I** gave no individual products.

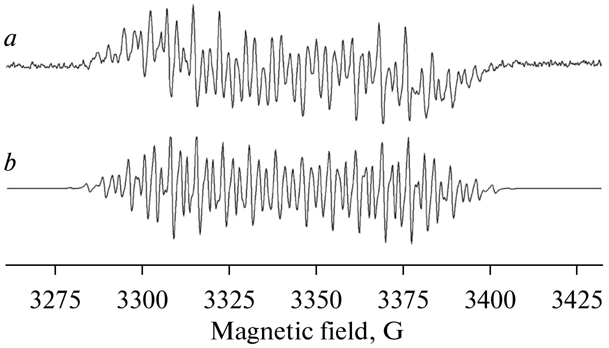


Fig. 2. (*a*) Experimental and (*b*) simulated EPR spectra for complex **I** (ether, 293 K).

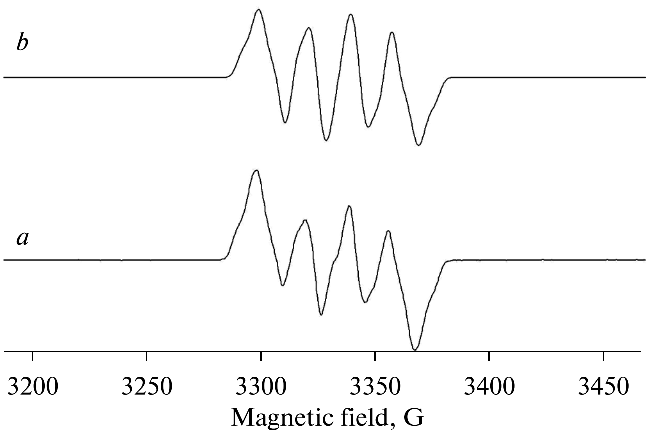


Fig. 3. (*a*) Experimental and (*b*) simulated EPR spectra for complex **II** (toluene, 293 K).

The structures of complexes **I** and **II** were determined by X-ray diffraction analysis (Fig. 1).The unit cell of structure **II** contains two crystallographically independent molecules of the complex. Both studied complexes are mononuclear, and the coordination node GaN$_2$Cl$_2$ in the complexes is a distorted tetrahedron. The angle between the planes GaN$_2$ and GaCl$_2$ varies from 88.5° to 89.4°. In both complexes the Ga atoms deviate from a nearly planar diimine fragment NCCN by no more than 0.22 Å.

The X-ray diffraction data confirm the radical anion nature of the ligands. The C–C distances in the central NCCN fragment (Table 2) are somewhat shortened compared to those in neutral diimines: both free DAB$^{\text{Me,Mes}}$ (1.500(2) Å [35]) and BIAN$^{\text{Dipp}}$ (1.534(6) Å [36]) and those coordinated to gallium(III) in complex [Ga(DAB$^{\text{H,Dipp}}$)Cl$_2$][GaCl$_4$] (1.478(8) Å [34]). On the contrary, the C–N distances in compounds **I** and **II** (average 1.349 and 1.334 Å) are somewhat elongated compared to the C=N double bonds in the free ligands (~1.28 Å). Similar C–C and C–N bond lengths in the central NCCN fragment are observed for the earlier described radical anion gallium complexes.

The radical anion nature of the diazabutadiene ligand in compounds **I** and **II** was confirmed by the EPR data for solutions (Figs. 2, 3). The obtained spectra were simulated using the Simfoniya program (Table 3). Unlike the poorly resolved spectrum of iodide complex Ga(DAB$^{\text{H,Dipp}}$)I$_2$ [26, 32], the well resolved spectrum is observed for compound **I**. The hyperfine coupling constants for complex **II** are similar to those for the iodide analog. According to the

Table 3. Values of the *g* factor and hyperfine coupling constants (G) in the ESR spectra of complexes **I** and **II** and their analogs

Compound	g_{iso}	$a(^{69}Ga)$	$a(^{71}Ga)$	$a(^{14}N)$	$a(^{1}H)$	References
$Ga(DAB^{H,Mes})Cl_2$ (**I**)	2.0023	18.00	22.8	7.5 (2N)		this work
$Ga(DAB^{H,Dipp})I_2$	2.0036	~25	~25	~5 (2N)	4.6 (4H)	[32]
$Ga(BIAN^{Dipp})Cl_2$ (**II**)	2.0034	17.0	21.6	4.0 (2N)	~5	this work
$Ga(BIAN^{Dipp})I_2$	2.0063	17	20	5.5 (2N)	3.8 (2H)	[32]

data of EPR spectroscopy, an unpaired electron in compounds **I** and **II** is predominantly localized on the atoms of the organic ligand. It also can be concluded that impurities of the initial Co complexes are absent from the transmetallation products.

Thus, we found a convenient method for the synthesis of the gallium(III) complexes with the radical anion form of the 1,4-diaza-1,3-butadiene or acenaphthene-1,2-diimine ligands. The method is based on the transmetallation by gallium of the corresponding cobalt(II) complexes containing neutral diimine. The obtained complexes were characterized by X-ray diffraction analysis and EPR spectroscopy.

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REFERENCES

1. Johnson, L.K., Killian, C.M., and Brookhart, M., *J. Am. Chem. Soc.*, 1995, vol. 117, p. 6414.
2. Shaver, M.P., Allan, L.E.N., Rzepa, H.S., and Gibson, V.C., *Angew. Chem., Int. Ed. Engl.*, 2006, vol. 45, p. 1241.
3. Binotti, B., Carfagna, C., Zuccaccia, C., and Macchioni, A., *Chem. Commun.,* 2005, p. 92.
4. Sprengers, J.W., de Greef, M., Duin, M.A., and Elsevier, C.J., *Eur. J. Inorg. Chem.,* 2003, p. 3811.
5. Heumann, A., Giordano, L., and Tenaglia, A., *Tetrahedron Lett.*, 2003, vol. 44, p. 1515.
6. Dieck, H. and Klaus, J., *J. Organomet. Chem.*, 1983, vol. 246, p. 301.
7. Gorls, H., Neumuller, B., Scholz, A., and Scholz, J., *Angew. Chem., Int. Ed. Engl.*, 1995, vol. 34, p. 673.
8. Brown, D.S., Decken, A., Schnee, C.A., and Cowley, A.H., *Inorg. Chem.*, 1995, vol. 34, p. 6415.
9. Chen, R. and Tatsumi, K., *J. Coord. Chem.*, 2002, vol. 55, p. 1219.
10. Kajita, Y., Ogawa, T., Matsumoto, J., and Masuda, H., *Inorg. Chem.*, 2009, vol. 48, p. 9069.
11. Kreisel, K.A., Yap, G.P.A., Dmitrenko, O., et al., *J. Am. Chem. Soc.*, 2007, vol. 129, p. 14162.
12. Shen, J., Yap, G.P.A., Werner, J.-P., and Theopold, K.H., *Chem. Commun.*, 2011, vol. 47, p. 12191.
13. Baker, R.J. and Jones, C., *Coord. Chem. Rev.*, 2005, vol. 249, p. 1857.
14. Hill, N.J., Vargas-Baca, I., and Cowley, A.H., *Dalton Trans.*, 2009, p. 240.
15. Fedushkin, I.L., Lukoyanov, A.N., Ketkov, S.Y., et al., *Chem. Eur. J.*, 2007, vol. 13, p. 7050.
16. Liddle, S.T., McMaster, J., Mills, D.P., et al., *Angew. Chem., Int. Ed.*, 2009, vol. 48, p. 1077.
17. Jones, C., Stasch, A., and Woodul, W.D., *Chem. Commun.*, 2009, p. 113.
18. Fedushkin, I.L., Lukoyanov, A.N., Tishkina, A.N., et al., *Organometallics*, 2011, vol. 30, p. 3628.
19. Liu, Y., Li, S., Yang, X.-J., et al., *J. Organomet. Chem.*, 2011, vol. 696, p. 1450.
20. Sanden, T., Gamer, M.T., Fagin, A.A., et al., *Organometallics*, 2012, vol. 31, p. 4331.
21. Gordon, A. and Ford, R., *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.
22. Rosa, V., Gonzalez, P.J., Aviles, T., et al., *Eur. J. Inorg. Chem.*, 2006, p. 4761.
23. Rosa, V., Carabineiro, S.A., Aviles, T., et al., *J. Organomet. Chem.*, 2008, vol. 693, p. 769.
24. Sheldrik, G.M., *SADABS. Program for Empirical X-ray Absorption Correction*, Bruker, 1990–2010.
25. *SHELXTL. Version 6.22*, Madison (WI, USA): Bruker, 2005.
26. Pott, T., Jutzi, P., Kaim, W., et al., *Organometallics*, 2002, vol. 21, p. 3169.

27. Baker, R.J., Farley, R.D., Jones, C., et al., *Dalton Trans.*, 2002, p. 3844.
28. Baker, R.J., Jones, C., Kloth, M., and Mills, D.P., *New J. Chem.*, 2004, vol. 28, p. 207.
29. Baker, R.J., Jones, C., Mills, D.P., et al., *Inorg. Chim. Acta*, 2008, vol. 361, p. 427.
30. Schmidt, E.S., Jockisch, A., and Schmidbaur, H., *J. Am. Chem. Soc.*, 1999, vol. 121, p. 9758.
31. Schmidt, E.S., Jockisch, A., and Schmidbaur, H., *Dalton Trans.*, 2000, p. 1039.
32. Baker, R.J., Farley, R.D., Jones, C., et al., *Chem. Eur. J.*, 2005, vol. 11, p. 2972.
33. Clyburne, J.A.C., Culp, R.D., Kamepalli, S., et al., *Inorg. Chem.*, 1996, vol. 35, p. 6651.
34. Jenkins, H.A., Dumaresque, C.L., Vidovic, D., and Clyburne, J.A.C., *Can. J. Chem.*, 2002, vol. 80, p. 1398.
35. Schaub, T. and Radius, U., *Z. Anorg. Allg. Chem.*, 2006, vol. 632, p. 807.
36. Fedushkin, I.L., Chudakova, V.A., Fukin, G.K., et al., *Russ. Chem. Bull.*, 2004, vol. 53, p. 2744.

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