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Peroxido Complexes of Vanadium(V) as Ligands. Crystal Structures of $[Cd(NH_3)_6][\{VO(O_2)_2(OH)\}_2\{\mu\text{-}Cd(NH_3)_4\}]$ and $[\{VO(O_2)_2(Im)\}_2\{\mu\text{-}Cu(Im)_4\}]$ (Im = Imidazole)

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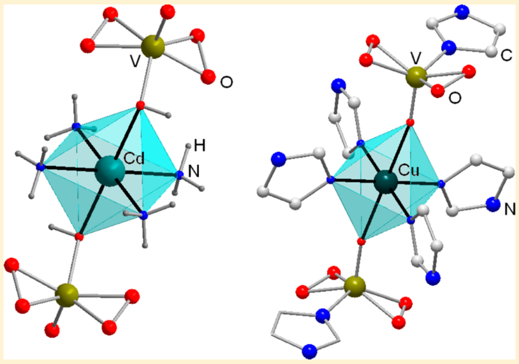
S *Supporting Information*

ABSTRACT: Two novel heterometallic complexes $[Cd(NH_3)_6][\{VO(O_2)_2(OH)\}_2\{\mu\text{-}Cd(NH_3)_4\}]$ (**2**) and $[\{VO(O_2)_2(Im)\}_2\{\mu\text{-}Cu(Im)_4\}]$ (**3**) (Im = imidazole) containing peroxidovanadium complexes as metalloligands were prepared and characterized by spectral methods. X-ray single-crystal analysis revealed the presence of unique trinuclear complexes in the crystal structures of **2** and **3**. The structure of **2** contains an anionic complex, whose two $\{VO(O_2)_2(OH)\}^{2-}$ ions are interconnected by a $\{\mu\text{-}Cd(NH_3)_4\}^{2+}$ group. Compound **3** is a trinuclear neutral complex comprising two $\{VO(O_2)_2(Im)\}^{-}$ ions and a single bridging $\{\mu\text{-}Cu(Im)_4\}^{2+}$ group. The bonding via an equatorial OH^- ligand in **2** and via a doubly bonded apical oxygen atom in **3** represents coordination modes previously unobserved for diperoxidovanadium complexes. Compared with complex **2**, density functional theory studies reported decreased Cu−μ-O bond orders and increased μ-O−V bond orders in **3**, in accordance with the expected Jahn−Teller distortion of the latter complex.



INTRODUCTION

During recent decades, compounds containing polyanions or complexes coordinated to other transition metal centers, forming thus heterometallic clusters or polymers, have been intensively studied. This research was motivated by a considerable potential of these compounds in the construction of materials having useful magnetic, luminescent, and/or catalytic properties. Vanadium polyanions are often participants in forming such heterometallic complexes. There are many examples of isopolyvanadate (e.g., $V_4O_{12}{}^{4-}$, $H_nV_{10}O_{28}{}^{(6-n)-}$)[1] and heteropolyvanadate ions[2] coordinated to transition-metal centers; however, only a limited number of compounds containing vanadium(V) complexes as ligands have been isolated so far. Examples of the last type of compounds are vanadium fluorido oxido complexes coordinated to copper[3] or silver centers,[4] heterometallic V−Fe compounds,[5] heterometallic V(V)/M (M = Na, K, Cs) coordination polymers,[6] and heterometallic complexes involving vanadium(V) and rhenium(VII) centers.[7]

Peroxidovanadium complexes have been intensively studied during recent decades thanks to their importance in biological systems (enzymes−vanadium haloperoxidases, insulin mimetic properties, antitumor activity, etc.)[8] and to their catalytic activity in many organic reactions.[9] To the best of our knowledge, however, only one example of a peroxidovanadium complex coordinated to another transition-metal central atom is currently known−in the $[\{VO(O_2)_2(NH_3)\}_2\{\mu\text{-}Cu(NH_3)_4\}]$ (**1**)[10] trinuclear heterometallic neutral complex, two $\{VO(O_2)_2(NH_3)\}^-$ ions are bridged by a $\{\mu\text{-}Cu(NH_3)_4\}^{2+}$ group. The bridge is of the Cu−(O$_2$)−V type with a μ-η^1:η^2-bonded peroxido ligand. Inspired by the existence of this complex, we tried to synthesize other heterometallic compounds containing peroxidovanadium complexes as ligands. Such attempts proved to be successful, and we present their results here. Two novel trinuclear complexes were prepared and characterized. In addition, new modes of coordination of peroxidovanadium fragment to the central atoms, namely, through either a doubly bonded oxygen or through an equatorial OH^- ligand, were observed.

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EXPERIMENTAL SECTION

Materials. Vanadium pentoxide was prepared by thermal decomposition (at 500 °C) of previously purified ammonium trioxovanadate. All other chemicals were of analytical grade and were used as supplied by Aldrich, Lachema, and Penta.

Synthesis of $[Cd(NH_3)_6][\{VO(O_2)_2(OH)\}_2\{\mu\text{-}Cd(NH_3)_4\}]$ **(2)**. Cadmium hydroxide was prepared by reacting the solution of $CdCl_2 \cdot 2.5H_2O$ (7.80 g, 34.2 mmol, in 20.0 mL of water) with a solution of sodium hydroxide (2.72 g, 68.0 mmol in 25.0 mL of H_2O). A precipitate was obtained, which was thoroughly decanted and filtered. To the freshly prepared $Cd(OH)_2$, ammonia solution (w = 25.0%, 50.0 mL, 667 mmol) and solid NH_4VO_3 (4.00 g, 34.2 mmol) were added. After complete dissolution, hydrogen peroxide (w = 30.0%, 6.00 mL, 58.8 mmol) was introduced. Finally, acetone (3.0 mL) was added to the yellow solution, which was set aside for crystallization at 5 °C. Yellow crystals were isolated after 24 h and dried at 5 °C. Anal. Calcd for $Cd_2H_{32}N_{10}O_{12}V_2$: Cd, 32.5; V, 14.7; O_2^{2-}, 18.5. Found: Cd, 32.2; V, 14.7; O_2^{2-}, 18.7%.

Synthesis of $[\{VO(O_2)_2(Im)\}_2\{\mu\text{-}Cu(Im)_4\}]$ **(3)**. Vanadium pentoxide (181 mg, 1.00 mmol) was dissolved in a solution of hydrogen peroxide (w = 3.00% in water, 11.0 mL, 10 mmol). A solution of copper(II) chloride dihydrate (171 mg, 1.00 mmol) and imidazole (Im) (614 mg, 9.02 mmol) in water (10.0 mL) was added to the solution of V_2O_5 under continuous stirring and cooling. The obtained dark blue solution was allowed to crystallize at 5 °C. Dark blue crystals were isolated after 12 h. Anal. Calcd for $CuC_{18}H_{24}N_{12}O_{10}V_2$: C, 29.5; H, 3.3; N, 22.9. Found: C, 29.6; H, 3.4; N, 23.2%.

Methods. *FT-IR and Raman Spectroscopy.* Fourier transform infrared (FT-IR) measurements were performed with a Nicolet 6700 FTIR, operating in the transmission range from 200 to 4000 cm^{-1}, collecting 64 scans with spectral resolution of 4 cm^{-1}. Spectra were recorded in Nujol and Fluorolube mulls or in KBr and polyethylene pellets. Raman spectra were registered at room temperature on an FT RA model FRA 106/S connected to an FTIR spectrometer FS 55 Equinox (Bruker); a Nd:YAG laser (1064 nm) was used.

^{51}V NMR Analysis. ^{51}V NMR spectra of aqueous solutions in 5 mm tubes were measured at 278 K on a Varian Mercury Plus 300 MHz spectrometer operating at 78.94 MHz (^{51}V) without locking on D_2O. Chemical shifts are in ppm relative to a $VOCl_3$ external reference.

Elemental Analysis. The elemental analyses of C, H, and N were performed on a Vario MIKRO cube (Elementar). Vanadium(V) was determined by titration with $FeSO_4$; peroxidic oxygen was determined by manganometric titration. The cadmium content was estimated by complexometric titration.

Thermogravimetric Analyses. Differential thermal analysis (DTA) and thermogravimetric (TG) curves were registered on Derivatograf Q 1500 D (MOM, Hungary). Thermal analysis was performed in air atmosphere, sample mass 100 mg, heating rate of 2.5 °C min^{-1} in the temperature range of 20−500 °C.

Computational Details. DFT calculations of **2** and **3** were carried out on the Fermi cluster at the J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i. Cartesian coordinates necessary for computational studies were exported from the solid-state geometries and were used without further geometry optimization. The cationic part of structure **2** was discarded, and the remaining trinuclear moiety was treated as a dianion; the solid-state structure of **3** was expanded into space group $P\bar{1}$ to obtain the symmetrically dependent part of the molecule. DFT results were obtained by employing Gaussian 09, Revision C.01,[11] the M06 functional,[12] and the QVZP basis set[13] for all atoms; the point group C_i was assumed for both cases. Natural bond order (NBO) studies were carried out using the NBO 3.1 program directly integrated in Gaussian as link 607.

X-ray Crystallography. Diffraction data for **2** were collected on a KUMA KM-4 κ-axis diffractometer using a graphite monochromated Mo Kα radiation (λ = 0.710 73 Å) and equipped with an Oxford Cryosystem LT-device. The ω scan technique with different κ and φ offsets for covering an independent part of reflections in the 2°−25° θ range was used. The intensity data were corrected for absorption effects using a multiscan procedure, and an empirical absorption correction was applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm (CrysAlis RED (Oxford Diffraction, U.K.) program). Cell parameters were refined from all strong reflections. Data reduction was carried out using the CrysAlis RED (Oxford Diffraction, U.K.) program.

A suitable single crystal of **3** was mounted onto a glass rod. Diffraction data were collected on a Nonius KappaCCD diffractometer (Mo Kα radiation, λ = 0.710 73 Å) equipped with a Bruker APEX-II CCD detector. Data were processed using the Bruker SAINT program package.[14]

The phase problem was solved by direct methods (SHELXS-97)[15] and refined by full matrix least-squares on F^2 (SHELXL-97).[16] Figures for publication were prepared with Diamond.[17] Crystal data and structure determination summaries for **2** and **3** are listed in Table 1.

Table 1. Crystal Data and Structure Refinement for 2 and 3

	2	3
empirical formula	$Cd_2H_{32}N_{10}O_{12}V_2$	$CuC_{18}H_{24}N_{12}O_{10}V_2$
M_r	691.04	733.91
temperature (K)	120(2)	150(1)
crystal system, space group	triclinic, $P\bar{1}$ (No. 2)	triclinic, $P\bar{1}$ (No. 2)
a (Å)	7.4932(2)	8.3596(3)
b (Å)	7.5385(2)	8.9885(3)
c (Å)	10.6984(3)	9.9801(3)
α (deg)	82.906(3)	87.287(2)
β (deg)	87.456(2)	66.7094(16)
γ (deg)	61.540(3)	88.053(2)
volume of unit cell (Å^3)	527.15(2)	687.93(4)
Z	1	1
calculated density (g/cm^3)	2.1767	1.7714
R_1[a,b]	0.0176	0.0301
wR_2[c]	0.0476	0.0767
R indices (all data)	0.0182	0.0377

[a] $I > 2\sigma(I)$. [b] $R_1 = 100\Sigma(||F_0| - |F_c||)/\Sigma|F_0|$. [c] $wR_2 = 100[\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_0^2) + [(ap)^2 + bp]]$, where $p = [\max(F_0^2, O) + 2F_c^2]/3$, a and b are constants.

RESULTS AND DISCUSSION

Synthesis, Spectroscopy, and Thermal Decomposition. To achieve a direct ligation of peroxidovanadium complexes to other metal centers, only complexes with vacant coordination sites or complexes having their coordination sites occupied by weakly bonded ligands can be used. In the case of **2** we used an ammonia solution of Cd(II) containing $[Cd(NH_3)_4]^{2+}$ and/or $[Cd(NH_3)_4(H_2O)_2]^{2+}$ cations[18] and peroxide−vanadium solution, where pentagonal pyramidal species $[VO(O_2)_2(OH)]^{2-}$ and $[VO(O_2)_2(H_2O)]^{-}$ were present.[19]

The yellow crystals of **2** undergo hydrolysis in aqueous solution, forming a white precipitate. In ammonia solution of **2**, where the hydrolysis is suppressed, the ^{51}V NMR spectrum exhibits three signals, which can be assigned to $[VO_2(O_2)(OH)]^{2-}$ (−625 ppm), $[VO(O_2)_2(NH_3)]^{-}$ (−747 ppm), and $[VO(O_2)_2(OH)]^{2-}$ (−765 ppm), the last being the dominant species (88% of vanadium) (Figure 1a).[20]

The dark blue crystals of **3** are sparingly soluble in water. The ^{51}V NMR spectrum of **3** exhibited only one sharp signal at −752 ppm (Figure 1b), which was unambiguously assigned to the $[VO(O_2)_2(Im)]^{-}$ ion.[21] This is evidence for the dissociation of $\{\mu\text{-}Cu(Im)_4\}^{2+}$ from the rest of molecule,

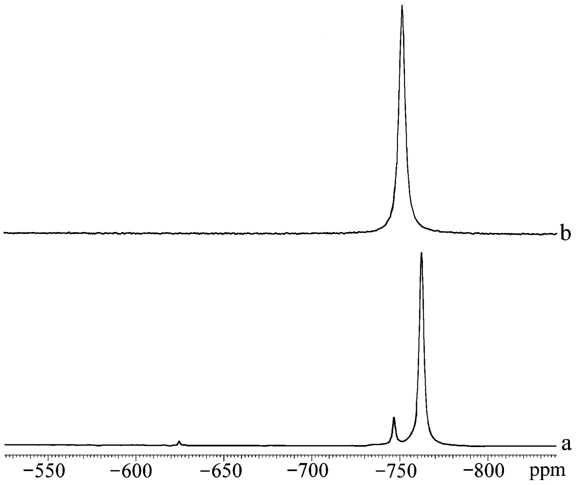

Figure 1. ^{51}V NMR spectra of saturated solutions of **2** (a) and **3** (b). Compound **2** was measured in aqueous ammonia solution (w = 5%), compound **3** in aqueous solution.

since the NMR signal was not broadened due to the proximity of the paramagnetic Cu^{2+} center.

Vibrational spectra of **2** (Table 2 and Supporting Information, Figure S1) exhibit typical bands of ammine complexes.[22] The characteristic bands of the $VO(O_2)_2$ moiety were observed at the expected positions: $\nu(V{=}O)$ at ~950 cm^{-1}, $\nu(O_p{-}O_p)$ at ~870 cm^{-1}, and $\nu(V{-}O_p)$ at ~610 and 520 cm^{-1}.[23]

Table 2. Characteristic Bands in Vibrational Spectra of 2

IR [cm^{-1}]	Raman [cm^{-1}]	assignment
3334s	3324m	$\nu_{as}(NH_3)+\nu_s(NH_3)$
3257w	3257m	$\nu_{as}(NH_3)+\nu_s(NH_3)$
3207w		$\nu_{as}(NH_3)+\nu_s(NH_3)$
3170m	3170m	$\nu(OH)$
1615sh	1621w	$\delta_{as}(HNH)$
1598m		$\delta_{as}(HNH)$
1197m		$\delta_s(HNH)$
1157s	1150w	$\delta_s(HNH)$
952vs	950vs	$\nu(V{=}O)$
885s		$\nu(O_p{-}O_p)$
870vs	877vs	$\nu(O_p{-}O_p)$
857m		$\nu(O_p{-}O_p)$
650sh		$\rho_r(NH_3)$
609vs	610m	$\nu(V{-}O_p)$
532m	521vvs	$\nu(V{-}O_p)$
471w	470m	$\nu(V{-}OH)$
363w	322s	$\nu(Cd{-}N)$
305s	306s	$\nu(Cd{-}N)$

The assignment of the bands corresponding to the coordinated imidazole in **3** (Table 3) was accomplished according to ref 24, where the interpretation of the IR spectra was supported by DFT calculations. The bands assigned to the $VO(O_2)_2$ moiety were again observed in the expected ranges (Table 3; Supporting Information, Figure S2). The band at ~490 cm^{-1} was assigned to V−N stretching, analogously to the previous assignment for $\{VO(O_2)_2(NH_3)\}^-$.[25]

The thermal decomposition of **2** is a two-step process (Figure 2). The first step on the TG curve (20−200 °C; calc. mass loss 31.6%; found 31.3%) can be described by eq 1.

Table 3. Characteristic Bands in Vibrational Spectra of 3

IR [cm^{-1}]	Raman [cm^{-1}]	assignment
3264m	3276w	$\nu(NH)$
3160w	3157w	$\nu(CH)$
3132s	3133vs	$\nu(CH)$
3123s	3124s	$\nu(CH)$
3111s	3068m	$\nu(CH)$
3062m	3058w	$\nu(CH)$
2964m	2961m	$\nu(CH)$
2879m	2873m	$\nu(CH)$
1532m	1525w	$\nu(CC)$, $\nu(CN)$
1500m	1487m	$\nu(CC)$, $\nu(CN)$
1451w	1445w	$\nu(CC)$, $\nu(CN)$
1424m	1417s	$\delta(NH)$, $\nu(CC)$, $\nu(CN)$
1328s	1320s	$\delta(CH)$, $\nu(CN)$
1268m	1255s	$\delta(CH)$
1171m	1163m	$\nu(CC)$, $\nu(CN)$, $\delta(CH)$
1146m	1139s	$\nu(CC)$, $\nu(CN)$, $\delta(CH)$
1132m		$\nu(CC)$, $\nu(CN)$, $\delta(CH)$
1068vs	1086s	$\nu(CC)$, $\nu(CN)$, $\delta(CH)$
970s		$\nu(V{=}O)$
963s	956vs	$\nu(V{=}O)$
885vs	881vs	$\nu(O_p{-}O_p)$
862s		$\nu(O_p{-}O_p)$
665s		$\tau(ring)$[a]
649m	644m	$\nu(V{-}O_p)$
614s	609m	$\pi(NH)$[a]
545m	537vs	$\nu(V{-}O_p)$
496m	484s	$\nu(V{-}N)$
286s	293w	ν_{as} + ν_s (Cu−N)
274sh	276s	ν_{as} + ν_s (Cu−N)
252s	250m	ν_{as} + ν_s (Cu−N)

[a] τ = torsion, π = out of plane bending.

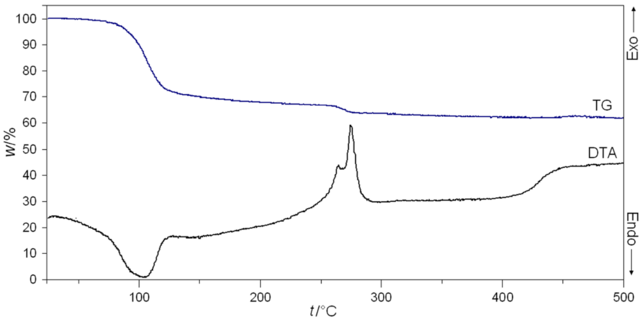

Figure 2. TG and DTA curves of **2**.

$$[Cd(NH_3)_6][\{VO(O_2)_2(OH)\}_2\{\mu\text{-}Cd(NH_3)_4\}] \rightarrow Cd_2(NH_3)_2V_2O_7 + 8NH_3 + 2O_2 + H_2O \quad (1)$$

This reaction is expressed on the DTA curve by an endothermic peak at 105 °C. The IR spectrum of the product obtained by interrupting the thermal decomposition at ~180 °C still exhibits the characteristic bands of coordinated ammonia molecules (at 1597 and 1207 cm^{-1}). The second step of the decomposition (200−400 °C) is accompanied by two exothermic peaks at 265 and 275 °C and corresponds to the release of the remaining ammonia molecules (calc. mass loss 36.5%; found 36.9%) (eq 2). The final solid product was confirmed by X-ray powder diffraction.[26] Because of the violent decomposition of **3** under thermal treatment, DTA and TG curves for **3** were not measured.

$$Cd_2(NH_3)_2V_2O_7 \rightarrow Cd_2V_2O_7 + 2NH_3 \qquad (2)$$

Description of the Crystal Structures. Crystal data and structure refinement of compounds **2** and **3** are in Table 1.

Compound **2** crystallizes in a triclinic lattice, space group $P\bar{1}$, having one $[Cd(NH_3)_6]^{2+}$ cation and one $[\{VO(O_2)_2(OH)\}_2\{\mu\text{-}Cd(NH_3)_4\}]^{2-}$ anion residing in the unit cell. The $[\{VO(O_2)_2(OH)\}_2\{\mu\text{-}Cd(NH_3)_4\}]^{2-}$ ion of C_i symmetry is a trinuclear heterometallic anionic complex consisting of two $\{VO(O_2)_2(OH)\}^-$ ions bridged by a $\{\mu\text{-}Cd(NH_3)_4\}^{2+}$ group (Figure 3). The angle of the Cd–O–V bridging group is 120.2(2)°.

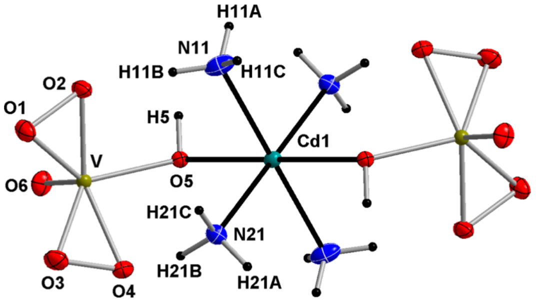

Figure 3. Molecular structure of $[\{VO(O_2)_2(OH)\}_2\{\mu\text{-}Cd(NH_3)_4\}]^{2-}$ anion in the crystal structure of **2**. Selected bond lengths (Å) (V–O1, 1.8952(2); V–O2, 1.8900(2); V–O3, 1.8769(19); V–O4, 1.8880(2); V–O5, 1.9612(2); V–O6, 1.6122(2); O1–O2, 1.4632(3); O3–O4, 1.4683(4); Cd1–O5, 2.4202(2); O5–H5, 0.8887(1)) and angles (deg) (O1–V–O6, 104.662(9); O2–V–O6, 106.771(1); O3–V–O6, 106.112(1); O4–V–O6, 107.000(1); O5–V–O6, 103.846(1); Cd1–O5–V, 120.224(9)). Thermal ellipsoides are drawn at the 50% probability level.

Both hexacoordinated vanadium atoms adopt a distorted pentagonal pyramidal environment filled by the apical oxido ligand, the four peroxido oxygen atoms, and one oxygen atom from the equatorial OH^- ligand. The vanadium atom is displaced by 0.5125(5) Å from the pentagonal pseudoplane toward the oxido ligand. The Cd1 atom is square planar coordinated by four ammine ligands, and the coordination about central atom is completed to tetragonal bipyramid by two bridging OH^- ligand. The crystal structure of **2** is stabilized by electrostatic interactions and N–H···O hydrogen bonds (Supporting Information, Table S1).

The protonation of V–O bonds is an important phenomenon, since it is very probably involved in catalysis by vanadium haloperoxidases,[20b] enzymes from marine algae, some terrestrial lichens, and fungi. More specifically, the comparison of structures of not very numerous Cd–O–V compounds has clearly shown the differences between V–O–Cd and V–OH–Cd bonds. For example, for $[\{Cd(bpy)_2\}_2V_4O_{12}]$[27] and $[\{Cd(phen)_2\}_2V_4O_{12}]\cdot 5H_2O$[28] the average bond parameters $d(V\text{–}O(\text{–}Cd)) = 1.663$ Å, $d(Cd\text{–}O(\text{–}V)) = 2.294$ Å, and $\alpha(V\text{–}O\text{–}V) = 133.17°$ were observed, while for **2** we found $d(V\text{–}OH(\text{–}Cd)) = 1.961(3)$ Å, $d(Cd\text{–}OH(\text{–}V)) = 2.420(2)$ Å, and $\alpha(Cd\text{–}O\text{–}V) = 120.224(9)°$. A characteristic feature upon protonation is the increase of the V–O bond length and decrease of the V–O–Cd angle (see also Bonding in 2 and 3).

Compound **3** crystallizes in the triclinic space group $P\bar{1}$, having two $\{VO(O_2)_2(Im)\}^-$ anions interconnected into a trinuclear neutral complex of C_i symmetry through one $\{\mu\text{-}Cu(Im)_4\}^{2+}$ group with square planar geometry (Figure 4). The copper(II) atom is hexacoordinated, with four nitrogen atoms from equatorial imidazole ligands and two axial oxygen atoms originating from the $\{VO(O_2)_2(Im)\}^-$ anions.

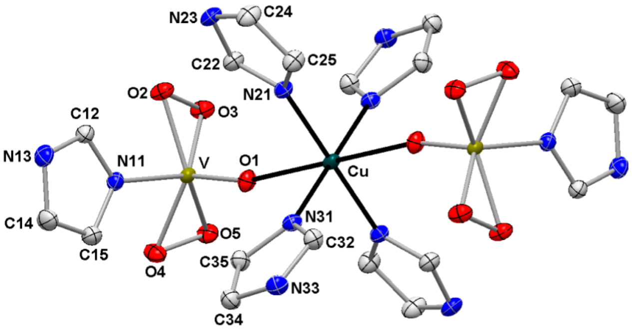

Figure 4. Molecular structure of **3**. Selected bond lengths (Å) (V–O1, 1.6120(13); V–O2, 1.8637(13); V–O3, 1.8761(16); V–O4, 1.8576(15); V–O5, 1.9053(17); V–N11, 2.0967(19); O2–O3, 1.4661(2); O4–O5, 1.4637(24); Cu–O1, 2.4421(1)) and angles (deg) (O1–V–O2, 108.885(7); O1–V–O3, 109.686(7); O1–V–O4, 113.270(7); O1–V–O5, 104.025(7); O1–V–N11, 97.133(7); V–O1–Cu, 165.768(8)). Hydrogen atoms are omitted for clarity. Thermal ellipsoides are drawn at the 50% probability level.

The geometry of the $\{VO(O_2)_2(Im)\}^-$ anions is pentagonal pyramidal. Four peroxido oxygen atoms and the imidazole nitrogen atom form the base of the distorted pyramid, while the doubly bonded oxygen atom occupies the apical position. The vanadium atom is displaced by 0.5371(3) Å from the pentagonal plane toward the oxido ligand. The supramolecular three-dimensional structure of **3** is formed by of hydrogen bonds (Supporting Information, Table S2) and π–π interactions formed between the molecules of $[\{VO(O_2)_2(Im)\}_2\{\mu\text{-}Cu(Im)_4\}]$.

There are two types of π–π interactions in the crystal structure of **3**, (i) between aromatic rings of imidazole ligands of the neighboring $\{VO(O_2)_2(Im)\}^-$ anions (Ct1–Ct1′) and (ii) between aromatic rings of imidazole ligands of the neighboring $\{\mu\text{-}Cu(Im)_4\}^{2+}$ groups (Ct2–Ct2′) (Figure 5). The distances between centroids are 3.61 Å for Ct1–Ct1′ and 3.77 Å for Ct2–Ct2′. The planes of interacting imidazole rings are parallel.

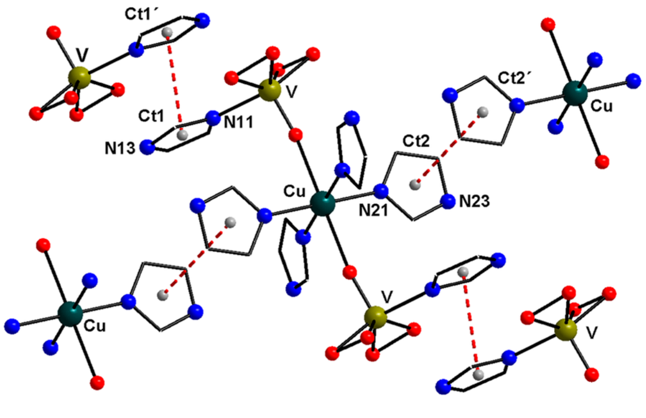

Figure 5. π–π interactions between aromatic rings of imidazole ligands in crystal structure of **3**.

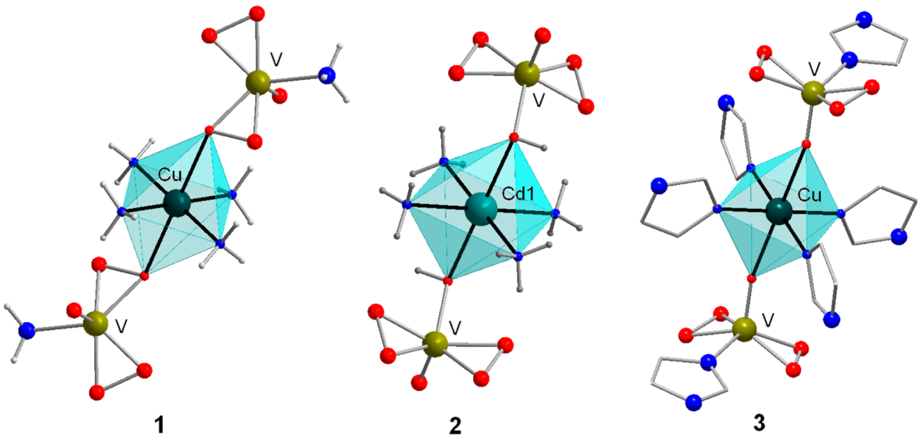

Figure 6. Trinuclear heterometallic complexes with diperoxidovanadium anion as ligand.

Table 4. Selected Interatomic Distances, Natural Charges, and Mayer Bond Orders around the Central Atoms in 2 (M = Cd) and 3 (M = Cu)

	d [Å]	natural charges	Mayer bond orders		
complex	(M−N; M−*μ*-O)	(M; N; *μ*-O)	M−N	M−*μ*-O	V−*μ*-O
2	2.33; 2.42	1.055; −0.960; −0.889	0.27	0.27	0.52
3	2.01; 2.44	1.161; −0.591; −0.579	0.29	−0.38	2.16

Trinuclear complexes **1**−**3** can be regarded as sandwich-type compounds, where two cations (anions) sandwich a central anion (cation).[29] The trinuclear heterometallic complexes in **1**, **2**, and **3** contain diperoxidovanadium anions, which exist in the solid state, namely, $HIm[VO(O_2)_2(Im)]$[21b] and $NH_4[VO(O_2)_2(NH_3)]$,[30] or are supposedly formed in solution ($[VO(O_2)_2(OH)]^{2-}$).[19] The latter ion is especially interesting, because it has yet never been observed as an isolated ion in the solid state. Compared with the structure of the original compounds, the structure of the diperoxidovanadium anions in **1** and **3** does not exhibit any significant differences. The typical pentagonal pyramidal structure, with two side-on bonded peroxido ligands and the vanadium atoms displaced toward the double-bonded oxygen atoms, is preserved; even the bond lengths and bond angles are very similar to the corresponding parameters of the parent compounds. We can therefore suppose that the structure of the elusive $\{VO(O_2)_2(OH)\}^{2-}$ ion as appearing in **2** represents its real structure also in solution. Interestingly, the V−OH bond is significantly shorter than the V−N bonds in **1** and **3** and is comparable with the V−F bonds in $K_2[VO(O_2)_2F]$[31] and $(NH_4)_2[VO(O_2)_2F]$.[32]

The comparison of three different modes of coordination of diperoxidovanadium complexes, namely, via equatorial peroxido oxygen atom (**1**), via equatorial OH^- ligand (**2**), and via doubly bonded oxygen atom (**3**), is presented in Figure 6. The hexacoordinated Cu and Cd atoms occupy the centers of slightly distorted tetragonal bipyramids. Because of the occurrence of the Jahn−Teller effect, the axial bonds for copper complexes are profoundly longer than their equatorial ones (Table 4). The bond lengths of axial bonds in **1** and **3** at about 2.4 Å are typical for Cu(II) complexes with a 4 + 2 coordination.[33]

Bonding in 2 and 3. For a better description of bonding in **2** and **3**, density functional theory (DFT) studies were carried out on the solid-state molecules. Our initial attempts to do some exploration of bonding by bond valence sum[34] (BVS) studies were abandoned due to the lack of bond valence parameters for O^-, which were vital to cope with the formal oxidation state (1−) of the peroxido group oxygens. Attempts to accomplish BVS with parameters of O^{2-} for the peroxido oxygens led to unbalanced charges for the whole molecules, and results obtained with them would have been nonphysical. Instead of BVS studies, bonding in both compounds was examined in detail by DFT computations, supplemented by NBO analyses.[35] Using the computational approach, only the centrosymmetric trinuclear moieties of **2** and **3** were investigated, which for complex **2** included only its anionic part.

A comparison of natural charges, bond distances, and Mayer bond orders[36] for **2** and **3** (cf. Table 4) clearly evidences the pronounced inequality of interatomic distances and bond orders around the copper atom in **2**.

According to NBO results, the atoms on inversion centers have their natural electron configurations: **2**—Cd: [Kr] $5s^{0.43}$ $4d^{9.99}$ $5p^{0.51}$ $5d^{0.01}$; **3**—Cu: [Ar] $4s^{0.29}$ $3d^{9.30}$ $4p^{0.42}$. In parallel with the trend of decreasing bond orders, the automatic search procedure of NBO reported no bonds to these metallic atoms, whereas it treated ligand coordination as ligand lone pair delocalizations into metallic acceptor orbitals.

As already observed for the case of titanocene complexes carrying an auxiliary hydroxo/alkoxo ligand,[37] the angle on the bridging oxygen/hydroxyl group had a significant impact on the extent of oxygen lone pair donation to the metallic d orbitals. Under ideal circumstances, such a donation should peak at a tetrahedral angle. However, steric requirements of real-world groups usually exhibit a tendency to increase the bending angle at the oxygen; for some very voluminous groups this angle may even become linear. Such a linear arrangement effectively decreases the internuclear repulsion between atoms. However, it concurrently impairs the efficiency of the O → M delocalization, decreasing thereby the M−O bond order and leading to the prolongation of the M−O interatomic distance.

The decrease of O → M delocalization was well-observable with the case of complex **3**, in which the presence of the bulkier imidazole ligands led to the increase of the Cu−O−V angle up to 165.77(9)°, whereas the corresponding Cd−μ-(OH)−V angle in **2** was as low as 120.2(2)°. The principal μ-O → Cd delocalizations in **2** occurred in the metallic 5s orbital, with energy of 117.00 kJ/mol, and the hybrid orbital formed from the combining the metallic $5p_x$ and $5p_z$ orbitals amounting to 125.62 kJ/mol. Because the decreased repulsion between the peroxidovanadium moiety and the equatorial ammine groups allowed the Cd−O−V angle to approach the ideal value, even the V−O bond exhibited a notable delocalization into the metallic $5p_x + 5p_z$ hybrid. The energy of the latter interaction amounted to 34.37 kJ/mol. The cadmium d orbitals were nearly fully occupied, and no major delocalization into them was reported by NBO. Concurrently, no significant back-donation from the cadmium atom was observed.

Being effectively a d^9 complex, complex **3** undergoes a Jahn−Teller distortion by prolonging its two axial Cu−μ-(O) bond distances. This bond elongation aids in alleviating the repulsion between the peroxido moiety and the equatorial Im ligands. However, steric demands of the equatorial Im ligands force the angle on the oxygen atoms to approach linearity, which subsequently decreases O → Cu delocalization energies and the corresponding bond orders. This decrease of bond orders could be traced well in NBO by the decreased values of respective delocalization energies. Since computation of paramagnetic **3** had to be carried out with a spin-unrestricted approach, α and β contributions were analyzed individually. The automatic search procedure of NBO reported no Cu−O bonds and treated all Cu−O interactions as donor lone pair delocalization into metallic acceptor orbitals. Two significant α delocalizations with energies of 58.56 and 28.51 kJ/mol and one single β delocalization amounting to 69.57 kJ/mol were present. On the other side, the Cu−N bonds were stronger. For NBO, their description posed a borderline case. For α-spin orbitals, no Cu−N bonds were reported, and major concurrent N → Cu delocalizations from one equatorial N-donor had energies of 64.92, 42.36, and 21.10 kJ/mol; the other symmetrically unrelated nitrogen donor had the same values of 66.64, 45.29, and 12.93 kJ/mol. The symmetrically related two donors exhibited the same values as their symmetric counterparts. For the β-spin orbitals, the formation of four Cu−N bonds were reported; however, their weak nature was apparent again from the decreased occupancy of the respective NBOs being as low as 0.96.

CONCLUSIONS

In the present study, the coordination ability of peroxidovanadium anions has been studied. Numerous synthetic attempts resulted in successful isolation of two novel heterometallic complexes $[Cd(NH_3)_6][\{VO(O_2)_2(OH)\}_2\{\mu\text{-}Cd(NH_3)_4\}]$ (**2**) and $[\{VO(O_2)_2(Im)\}_2\{\mu\text{-}Cu(Im)_4\}]$ (**3**). The prepared compounds were characterized by ^{51}V NMR, IR, and Raman spectroscopies, thermal analysis (complex **2**), and X-ray crystallography. An interesting structural feature in complex **2** is the presence of the elusive $\{VO(O_2)_2(OH)\}^{2-}$ ion, never yet observed as an isolated ion in a solid-state compound. Complexes **2** and **3** together with the previously described complex **1** are the only examples of peroxidovanadium species coordinated to another transition-metal center reported so far. These three complexes represent a complete set of monodentate coordination modes of the $VO(O_2)_2X$ fragments: via peroxido oxygen atom (**1**), equatorial X ligand (**2**), and terminal oxygen atom (**3**). DFT results for **2** show the presence of six comparably strong bonds to the cadmium atom. In complex **3**, where a Jahn−Teller distortion takes place, the apical Cu−O bonds are elongated, and compared with complex **1**, the Cu−O bond orders are decreased.

ASSOCIATED CONTENT

Supporting Information

Crystallographic information in CIF format (ICSD-427106 for **2** and CCDC 974520 for **3**), infrared and Raman spectra of **2** and **3**, tables of hydrogen bonds in **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Zhang, Y.; Zapf, P. J.; Meyer, L. M.; Haushalten, R. C.; Zubieta, J. *Inorg. Chem.* **1997**, *36*, 2159. (b) Hagrman, P. J.; Finn, R. C.; Zubieta, J. *Solid State Sci.* **2001**, *3*, 745 and citations therein. (c) Joniaková, D.; Gyepes, R.; Rakovský, E.; Schwendt, P.; Žúrková, L'.; Marek, J.; Mička, Z. *Polyhedron* **2006**, *25*, 2491. (d) Klištincová, L.; Rakovský, E.; Schwendt, P. *Inorg. Chem. Commun.* **2008**, *11*, 1140. (e) Li, T.; Lü, J.; Gao, S.; Li, F.; Cao, R. *Chem. Lett.* **2007**, *36*, 356. (f) Bartošová, L.; Padělková, Z.; Rakovský, E.; Schwendt, P. *Polyhedron* **2012**, *31*, 565 and citations therein. (g) Lan, Y. Q.; Li, S. L.; Wang, X. L.; Shao, K. Z.; Du, D. Y.; Su, Z. M.; Wang, E. B. *Chem.—Eur. J.* **2008**, *14*, 9999.

(2) For example: (a) Pan, C. L.; Xu, J. Q.; Sun, Y.; Chu, D. Q.; Ye, L.; Lu, Z. L.; Wang, T. G. *Inorg. Chem. Commun.* **2003**, *6*, 233. (b) Han, Z. G.; Wu, J. J.; Gao, Y. Z.; Zhai, X. L. *Aust. J. Chem.* **2011**, *64*, 197. (c) Pan, C. L.; Xu, J. Q.; Chu, D. Q.; Li, G. H.; Lu, Z. L.; Yang, G. D. *Inorg. Chem. Commun.* **2003**, *6*, 939. (d) Luan, G. Y.; Li, Y. G.; Wang, E. B.; Han, Z. B.; Hu, C. W.; Hu, N. H.; Jia, H. Q. *J. Solid State Chem.* **2002**, *165*, 1. (e) Liu, C. M.; Zhang, D. Q.; Xiong, M.; Zhu, D. B. *Chem. Commun.* **2002**, *13*, 1416.

(3) Welk, M. E.; Norquist, A. J.; Stern, C. L.; Poeppelmeier, K. R. *Inorg. Chem.* **2000**, *39*, 3946.

(4) Senchyk, G. A.; Bukhan'ko, V. O.; Lysenko, A. B.; Krautscheid, H.; Rusanov, E. B.; Chernega, A. N.; Karbowiak, M.; Domasevitch, K. V. *Inorg. Chem.* **2012**, *51*, 8025.

(5) Bhattacharya, K.; Maity, M.; Mondal, D.; Endo, A.; Chaudhury, M. *Inorg. Chem.* **2012**, *51*, 7454.

(6) Gupta, S.; Kirillova, M. V.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L.; Kirillov, A. M. *Inorg. Chem.* **2013**, *52*, 8601.

(7) Chatterjee, P. B.; Abtab, Sk. Md. T.; Bhattacharya, K.; Endo, A.; Shotton, E. J.; Teat, S. J.; Chaudhury, M. *Inorg. Chem.* **2008**, *47*, 8830.

(8) (a) Posner, B. I.; Faure, R.; Burgess, J. W.; Bevan, A. P.; Lachance, D.; Zhang-Sun, G.; Fantus, I. G.; Ng, J. B.; Hall, D. A.; Lum, B. S.; Shaver, A. *J. Biol. Chem.* **1994**, *269*, 4596. (b) Djordjevic, C.; Wampler, G. L. *J. Inorg. Biochem.* **1985**, *25*, 51. (c) Gorzás, A.; Andersson, I.; Pettersson, L. *J. Inorg. Biochem.* **2009**, *103*, 517. (d) Gabriel, C.; Kioseoglou, E.; Venetis, J.; Psycharis, V.; Raptopoulou, C. P.; Terzis, A.; Voyiatzis, G.; Bertmer, M.; Mateescu, C.; Salifoglou, A. *Inorg. Chem.* **2012**, *51*, 6056. (e) Crans, D. C.; Smee, J. J.; Gaidamauskas, E.; Yang, L. *Chem. Rev.* **2004**, *104*, 849. (f) Rehder, D.; Časný, M.; Grosse, R. *Magn. Reson. Chem.* **2004**, *42*, 745. (g) Časný, M.; Rehder, D. *Dalton Trans.* **2004**, 839.

(9) (a) Conte, V.; Coletti, A.; Floris, B.; Licini, G.; Zonta, C. *Coord. Chem. Rev.* **2011**, *255*, 2165. (b) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101.

(c) Conte, V.; Floris, B. *Dalton Trans.* **2011**, *40*, 1419. (d) Conte, V.; Floris, B. *Inorg. Chim. Acta* **2010**, *363*, 1935. (e) Butler, A.; Clague, M. J.; Meister, G. E. *Chem. Rev.* **1994**, *94*, 625. (f) Brégeault, J.-M.; Vennat, M.; Salles, L.; Piquemal, J.-Y.; Mahha, Y.; Briot, E.; Bakala, P. C.; Atlamsani, A.; Thouvenot, R. *J. Mol. Catal. A: Chem.* **2006**, *250*, 177. (g) Conte, V.; Di Furia, F.; Moro, S. *J. Mol. Catal. A: Chem.* **1995**, *104*, 159. (h) Maurya, M. R.; Kumar, M.; Sikarwar, S. *React. Funct. Polym.* **2006**, *66*, 808. (i) Clague, M. J.; Keder, N. L.; Butler, A. *Inorg. Chem.* **1993**, *32*, 4754.

(10) Chrappová, J.; Schwendt, P.; Dudášová, D.; Tatiersky, J.; Marek, J. *Polyhedron* **2008**, *27*, 346.

(11) *Gaussian 09,* Revision C.01; Gaussian, Inc.: Wallingford, CT, 2009.

(12) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

(13) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(14) *SAINT*, Bruker AXS, Inc.: Madison, WI, 2001.

(15) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

(16) Sheldrick, G. M. *SHELXS-97 and SHELXL-97;* University of Göttingen: Göttingen, Germany, 1997.

(17) *DIAMOND,* Version 3.1i; Crystal Impact: Bonn, Germany, 2001.

(18) (a) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry;* 6th ed.; John Wiley & Sons: New York, 1999; p 600. (b) Holleman, A. F.; Wiberg, E. *Lehrbuch der Anorganischen Chemie. 101. Auflage;* Walter de Gruyter: Berlin, Germany, 1995; p 1374.

(19) Howarth, O. W.; Hunt, J. R. *J. Chem. Soc., Dalton Trans.* **1979**, 1388.

(20) (a) Tracey, A. S.; Wilsky, G. R.; Takeuchi, E. S. *Vanadium Chemistry, Biochemistry, Pharmacology and Practical Applications;* CRC Press: Boca Raton, FL, 2007; p 83. (b) Rehder, D. *Bioinorganic Vanadium Chemistry;* John Wiley & Sons, Chichester, U.K., 2008. (c) Jaswal, J. S.; Tracey, A. S. *Inorg. Chem.* **1991**, *30*, 3718.

(21) (a) Andersson, I.; Angus-Dunne, S. J.; Howarth, O. W.; Pettersson, L. *J. Inorg. Biochem.* **2000**, *80*, 51. (b) Crans, D. C.; Keramidas, A. D.; Hoover-Litty, H.; Anderson, O. P.; Miller, M. M.; Lemoine, L. M.; Pleasic-Williams, S.; Vandeberg, M.; Rossomando, A. J.; Sweet, L. J. *J. Am. Chem. Soc.* **1997**, *119*, 5447.

(22) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* 4th ed.; John Wiley & Sons: New York, 1986; p 191.

(23) Schwendt, P.; Volka, K.; Suchánek, M. *Spectrochim. Acta* **1988**, *44A*, 839.

(24) Morzyk-Ociepa, B.; Rózycka-Sokolowska, E.; Michalska, D. *J. Mol. Struct.* **2012**, *1028*, 49.

(25) Schwendt, P.; Pisárčik, M. *Collect. Czech. Chem. Commun.* **1982**, *47*, 1549.

(26) (a) Reseterič, J.; Schwendt, P.; Joniaková, D. *Acta Fac. Rerum Nat. Univ. Comenianae, Chim.* **1979**, *XVII*, 41. (b) Sokolova, E. V.; Egorov-Tismenko, Yu. K.; Simonov, M. A.; Krasnenko, T. I. *Kristallografiya* **1986**, *31*, 1222.

(27) Sun, X.-Z.; Wang, B.-Y.; Zhong, L.-Y. *Acta Crystallogr.* **2004**, *E60*, m1100.

(28) Qi, Y.; Wang, Y.; Li, H.; Cao, M.; Hu, C.; Wang, E.; Hu, N.; Jia, H. *J. Mol. Struct.* **2003**, *650*, 123.

(29) (a) Zhang, D.; Kong, L.; Zhao, Z.; Wang, P.; Chen, X. *Transition Met. Chem.* **2014**, article in press, DOI: 10.1007/s11243-014-9806-0. (b) Yamaguchi, S.; Kikukawa, Y.; Tsuchida, K.; Nakagawa, Y.; Uehara, K.; Yamaguchi, K.; Mizuno, N. *Inorg. Chem.* **2007**, *46*, 8502. (c) Shiga, T.; Ohba, M.; Ōkawa, H. *Inorg. Chem.* **2004**, *43*, 4435. (d) Danis, J. A.; Lin, M. R.; Scott, B. L.; Eichhorn, B. W.; Runde, W. H. *Inorg. Chem.* **2001**, *40*, 3389.

(30) Drew, R. E.; Einstein, F. W. B. *Inorg. Chem.* **1972**, *11*, 1079.

(31) Stomberg, R. *Acta Chem. Scand.* **1984**, *A38*, 223.

(32) Stomberg, R.; Olson, S. *Acta Chem. Scand.* **1984**, *A38*, 801.

(33) Murphy, B.; Hathaway, B. *Coord. Chem. Rev.* **2003**, *243*, 237.

(34) Altermatt, D.; Brown, I. D. *Acta Crystallogr.* **1985**, *B41*, 244.

(35) Foster, P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211.

(36) Mayer, I. *Int. J. Quantum Chem.* **1986**, *29*, 73.

(37) Gyepes, R.; Varga, V.; Horáček, M.; Kubišta, J.; Pinkas, J.; Mach, K. *Organometallics* **2010**, 3780.