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Copper(II), cobalt(II), manganese(II) and nickel(II) bis(hexafluoroacetylacetonate) complexes with *N*-vinylimidazole

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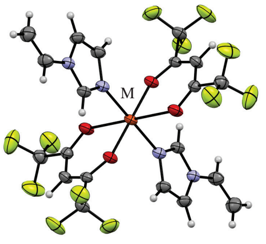
Two new manganese(II) and nickel(II) bis(hexafluoroacetylacetonate) complexes with *N*-vinylimidazole were synthesized and characterized by single crystal X-ray diffraction analysis, UV-VIS and IR spectroscopy. Their structures were compared with those of related copper(II) and cobalt(II) complexes. In the case of copper complex, the coordination site formed by hexafluoroacetylacetonate at the Cu^{2+} ion and nitrogen atoms of the two vinylimidazole cycles is slightly distorted, while in all the other considered complexes, this distortion is insignificant.



M = Cu, Co, Mn, Ni

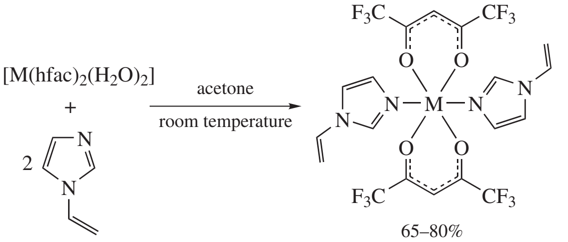
Keywords: metal complexes, hexafluoroacetylacetonates, crystal structure, X-ray, UV-VIS spectra.

Currently, quite a lot of theoretical and experimental data have been acquired on the physicochemical properties, composition, and structural features of transition metal complexes bearing chelating ligands (*e.g.*, β-diketonates).[1–6] The β-diketonates possess unique physicochemical features that allow them to be employed as inhibitors or catalysts of oxidation, addition and polymerization reactions. Interesting properties of these compounds include an increase in the saturated vapor pressure with increasing temperature and a thermal stability. Due to these properties, metal β-diketonates are widely used for the preparation of metal-containing coatings and films *via* a thermal deposition from the gas phase. Fluorinated β-diketonates of metals are superior in their useful properties as compared to their non-fluorinated analogs.[7] Various compounds, including acetone,[8] 4-aminopyridine,[9] and pyridine,[10] were employed as the organic ligands in such complexes.

The metal complexes with 1-vinylimidazole are of particular interest due to the wide range of their biological activity. Drugs based on these complexes were designed, *e.g.* the carbon monoxide antidote, Atsizol [bis(1-vinylimidazole)zinc diacetate],[11] and hematopoiesis stimulator, Kobazol [bis(1-isopropenylimidazole)-cobalt dichloride].[12] Many ongoing works are devoted to the synthesis of metal complexes containing vinylimidazole and to the study of their physicochemical properties, including magnetic ones.[13–17]

This work was aimed at the synthesis of copper(II), cobalt(II), manganese(II) and nickel(II) bis(hexafluoroacetylacetonate) (hfac) complexes with vinylimidazole and their structural study by the single crystal X-ray diffraction analysis and UV-VIS spectroscopy. The starting hexafluoroacetylacetonates, $[Cu(hfac)_2(H_2O)_2]$, $[Co(hfac)_2(H_2O)_2]\cdot H_2O$, $[Ni(hfac)_2(H_2O)_2]$, and $[Mn(hfac)_2(H_2O)_2]$, were prepared according to the known method.[18] Complexes **1**–**4** were synthesized in good yields *via* the reaction of corresponding hexafluoroacetylacetonates with 1-vinylimidazole in acetone solution (Scheme 1).[†]

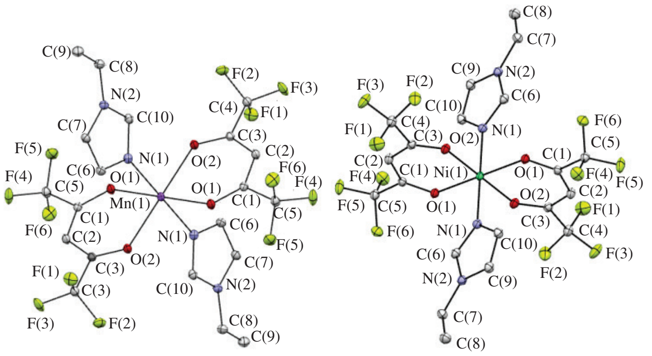
Figure 1 shows the molecular structures of complexes **3** and **4**,[‡] while those of complexes **1** and **2** have been reported in our previous works (CCDC 1031424 and 1031425, refcodes POTRIB and POTROH, respectively).[19,20] A bipyramidal coordination is realized in the molecules of complexes **1**–**4**. Their molecular structures possess a slightly distorted square planar coordination of four oxygen atoms of the two hexafluoroacetonate ligands, which is typical of the β-diketonate complexes of Cu, Co, Mn, and Ni.[1–6] In the case of compound **1**, the coordination site formed by the copper hexafluoroacetylacetonate and N(1) nitrogen atoms of the two imidazole rings is not planar and significantly distorted.[19] The difference in the Cu–O bond lengths is 0.309 Å: the Cu(1)–O(1) bond length is 2.325(1) Å for one diagonal, and that of Cu(1)–O(2) is 2.016(2) Å for the other; the O(1)–Cu(1)–O(2)



1 M = Cu **3** M = Mn
2 M = Co **4** M = Ni

Scheme 1

[†] See Online Supplementary Materials for the experimental details.



3 **4**

Figure 1 Molecular structure of complexes **3** and **4** showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) for compound **3**: Mn(1)–O(1) 2.205(1), Mn(1)–O(2) 2.160(1), Mn(1)–N(1) 2.217(1); and those for **4**: Ni(1)–O(1) 2.048(1), Ni(1)–O(2) 2.073(1), Ni(1)–N(1) 2.070(1). Selected angles (°) for **3**: O(1)–Mn(1)–O(2) 84.11(3), O(1)–Mn(1)–O(1) 180.00(1), O(1)–Mn(1)–N(1) 88.77(3); and those for **4**: O(1)–Ni(1)–O(2) 90.06(3), O(1)–Ni(1)–O(1) 180.00(1), O(1)–Ni(1)–N(1) 90.18(4).

and O(1)–Cu(1)–O(1) angles are 85.66(5) and 180.00(1)°, respectively.[19] The C–F bond lengths in CF_3 groups are in the range of 1.327(2)–1.332(2) Å. The oxygen atoms at the coordination rhombus lie strictly in the root-mean-square plane, whereas the deviations of carbon atoms from it do not exceed 0.158 Å. The chelate rings possess small kinks (7.39°) along the O···O line and lie in the equatorial plane.[19] In contrast to complex **1**, the coordination site distortion in complexes **2**–**4** is insignificant, while the differences in lengths for the Co–O, Mn–O and Ni–O bonds are 0.015, 0.045 and 0.025 Å, respectively.

The Co–O bond lengths in compound **2** are 2.098(1) Å for one[19] diagonal and 2.083(1) Å for the other,[20] the lengths of Mn–O diagonal bonds in complex **3** are 2.205(1) and 2.160(1) Å, and those of Ni–O bonds in complex **4** are 2.048(1) and 2.073(1) Å. The O(1)–M(1)–O(1) angles in compounds **1**–**4** are 180.00(1)°. The oxygen atoms of a slightly distorted coordination square in complexes **2**–**4** lie strictly in the mean-square plane, whereas the deviations of carbon atoms from it do not exceed 0.165, 0.235 and 0.140 Å for complexes **2**,[20] **3** and **4**, respectively. The chelate rings are in the equatorial plane and exhibit small kinks along the O···O line: 6.18, 11.04 and 7.66° for complexes **2**,[20] **3** and **4**, respectively. The imidazole ligands in the considered complexes are attached to the metal atom *via* the nitrogen atom and deployed perpendicular to the axial plane at 89.88, 89.75, 86.85 and 87.87° for complexes **1**,[19] **2**,[20] **3** and **4**, respectively. The lengths of equatorial coordination M–N bonds are within the usual limits typical of copper, cobalt, manganese and nickel complexes: 1.998(2) (**1**),[19] 2.119(2) (**2**),[20] 2.217(1) (**3**) and 2.070(1) Å (**4**).

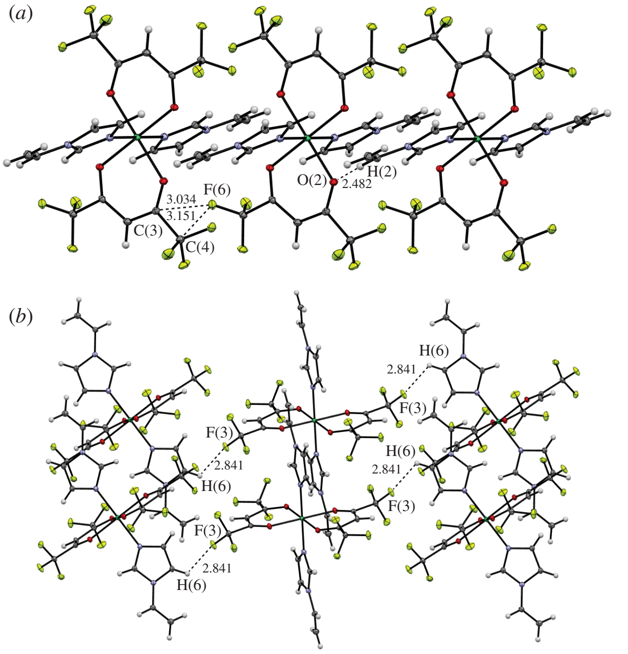


Figure 2 Crystal structure of complex **3**: (*a*) a fragment of the stack crystal structure and (*b*) a fragment of the crystal structure with interlayer binding.

Crystals of compounds **1**–**4** are isostructural. Endless stacks with the same orientation represent the architectural motif of complexes **1**–**4**. Figure 2 shows an example of such a structure for complex **3**. The stack is formed through the short intermolecular contacts between the fluorine atoms and carbon atoms of chelate cycle, F(6)···C(3) (3.034 Å), F(6)···C(4) (3.151 Å), and intermolecular O(2)···H(2) hydrogen bonds (2.484 Å) [see Figure 2(*a*)]. Interlayer binding arises due to the interaction of fluorine atom of one complex molecule with the hydrogen of imidazole cycle of the other: F(3)···H(6) (2.841 Å) [see Figure 2(*b*)].

Single crystal X-ray data on the structure of complexes **1**–**4** were consistent with the data acquired using methods of vibrational and electron spectroscopy. In the IR spectra of complexes **1**–**4**, a short-wavelength shift (10–30 cm^{-1}) of the absorption bands at 1495–1530 cm^{-1} corresponding to the stretching vibrations of imidazole ring relative to the absorption of ligands was observed, which suggests the formation of a coordination bond at the imidazole nitrogen atom of heterocycle: $N \rightarrow M$, where M is Cu, Co, Mn, or Ni.[21] In the electronic spectra of acetonitrile solutions of the considered complexes, absorption bands were detected in the range of 228–1090 nm (Table S1 in Online Supplementary Materials).

The electronic spectra of transition metal complexes are used to solve structural problems, since their structure is associated with the presence of partially or fully filled molecular orbitals. In the UV-VIS spectra of complexes **1**–**4**, two intense bands in the range of 228–231 nm arise due to $\pi \rightarrow \pi^*$ electron transitions,[3,4] and the shoulder in the range of 325–335 nm belongs to the $n \rightarrow \pi^*$ transition localized in the imidazole ring. The intense absorption bands at 310 [lg(ε) = 4.56] (**1**), 301 [lg(ε) = 4.58] (**2**), 308 [lg(ε) = 4.77] (**3**) and 316 nm [lg(ε) = 4.51] (**4**) are apparently related to a charge transfer between the orbitals localized at the N heteroatom of imidazole ring and Cu^{2+}, Co^{2+}, Mn^{2+} and Ni^{2+} ions.[16] In the visible region of 500–1100 nm (see Table S1), the bands of complexes **1**–**4** are characterized by relatively low values of the

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‡ *Crystal data for* **3**. $C_{20}H_{14}N_4F_{12}O_4Mn$, $M = 657.29$, monoclinic, space group $P2_1/c$, $a = 6.616(1)$, $b = 19.515(1)$ and $c = 9.222(1)$ Å, $\beta = 95.57(1)°$, $V = 1185.7(2)$ Å^3, $Z = 2$. At 100 K: $\mu = 0.689$ mm^{-1}, $d_{calc} = 1.841$ g cm^{-3}. Total 37916 reflections were collected, where 3492 reflections were independent; 187 refined parameters, $\sigma = 1.076$, and final R factor was 2.84 ($R_{int} = 0.0708$).

Crystal data for **4**. $C_{20}H_{14}N_4F_{12}O_4Ni$, $M = 661.04$, monoclinic, space group $P2_1/c$, $a = 6.627(1)$, $b = 18.893(2)$ and $c = 9.355(1)$ Å, $\beta = 96.19(1)°$, $V = 1164.5(2)$ Å^3, $Z = 2$. At 100 K: $\mu = 0.968$ mm^{-1}, $d_{calc} = 1.885$ g cm^{-3}. Total 37094 reflections were collected, where 3423 reflections were independent; 187 refined parameters, $\sigma = 1.057$, and final R factor was 2.67 ($R_{int} = 0.0654$).

Crystallographic data were collected on a Bruker D8 Venture diffractometer (MoKα radiation, $\lambda = 0.71073$) using the modes of φ and ω scans. The structures were solved and refined by direct methods using the set of SHELX programs.[25] The data were corrected for absorption effects using the multi-scan method (SADABS). Non-hydrogen atoms were refined anisotropically using SHELX.[25] All the hydrogen atoms were found *via* Fourier difference maps.

CCDC 1036429 and 1033038 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

molar extinction coefficients that is about 5–80 $dm^3 mol^{-1} cm^{-1}$ [lg(ε) of 1.54–0.84] due to the *d*→*d* electron transitions for transition metal ions possessing incompletely filled *d* shells.[22,23] The weak intensity of these transitions for the Cu^{2+}, Co^{2+}, Mn^{2+} and Ni^{2+} ions is due to the fact that they are forbidden by the selection rules. Arising of a band for the *d*→*d* transitions in the complexes can be explained by the 'partial mixing' of their *d* and *p* orbitals and by the transition of an electron from these orbitals to the *d* orbitals, which is not forbidden.[22] The recorded spectrum of complex **1** in the visible region is a wide band with the absorption maximum at 743 nm and shoulders at 446 nm in the low-frequency region and at 1034 nm, which refers to electronic *d*→*d* transitions of the Cu^{2+} ion (Figure S1). In the case of complex **2**, a distinct band was observed with the maximum at 509 nm and shoulder at 550 nm, shifted to the low-frequency region by 234 nm as compared to the spectrum of **1**, and a less intense absorption at 1089 nm (0.84) (Figure S2). The absorption bands in this region are also associated with the transitions between the *d*-orbitals of Co^{2+} ion. According to the theory of ligand field,[24] the splitting of *d* level of the central ion in a complex is associated with the removal of degeneracy under the influence of the surrounding ligands. The spectra of complexes **3** and **4** are similar to those of **1** and **2** (Figures S3 and S4).

In summary, the features of molecular and crystal structures of two new Mn and Ni hexafluoroacetonate complexes with *N*-vinylimidazole have been revealed by the single crystal X-ray diffraction analysis, and these data have been analyzed as a comparison with the similar Cu and Co complexes. The UV-VIS spectra of complexes **1–4** are characterized by the following types of electronic transitions: transitions between molecular orbitals due to an electron transfer from the *p*-orbital of the nitrogen heteroatom of vinylimidazole to the *d*-orbital of metal ions (charge transfer bands) and *d*→*d* transitions between the molecular orbitals of Cu, Co, Mn and Ni metal ions. The acquired data have supported the background information on the structure and properties of complexes of metal hexafluoroacetylacetonates with various ligands and may be useful for the studies in related fields.

All the measurements were performed using the equipment of the Baikal Center for Collective Use of the Siberian Branch of the Russian Academy of Sciences.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.03.040.

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