Inorganic Chemistry
Addition/Correction
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Correction to Synthesis and Properties of the Cyano Complex of Oxo-Centered Triruthenium Core $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(pyridine)_2(CN)]$

Hua-Xin Zhang,* Yoichi Sasaki,* Yi Zhang, Shen Ye, Masatoshi Osawa, Masaaki Abe, and Kohei Uosaki

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The original version of this paper has been revised in light of concerns raised by a reader. The manuscript has been revised to avoid decisive expression on π-donation from the cyano ligand and also to weaken relevant statements. The new version has changes to the Table of Contents and Abstract graphics, Synopsis, Abstract, sections of the Results and Discussion, and Supporting Information.

Page A (to be updated before publication). The Table of Contents and Abstract graphics have been replaced.

The Synopsis text "A new oxo-centered triruthenium(III) complex with cyanide as the terminal ligand has been prepared and characterized. Because of the electron-deficient nature of the oxo-triruthenium core, the cyano ligand was found to behave as a π-donor in addition to the usual character as a σ-donor. Molecular orbital calculations revealed that the cyano-coordinated triruthenium unit has a delocalized electronic structure, which is different from the localized structures of the CO-containing complexes." has been changed to "A new oxo-centered triruthenium(III) complex with cyanide as the terminal ligand has been prepared and characterized. The redox potentials of two processes of the cyanide complex are even more negative than those of the pyridine-containing complex. Molecular orbital calculations revealed that the cyano-coordinated triruthenium unit has a delocalized electronic structure, while the corresponding CO-containing complex takes a localized structure due to the strong π-back-donation to CO.".

The Abstract text "$[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$, indicating that the CN^- ligand acts as a π-donor as well as a σ-donor. This is in sharp contrast to the π-back-bonding to CO in $[Ru_3^{II,III,III}(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_2(CO)]$." has been changed to "$[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$. This is in sharp contrast to the positive shifts of the corresponding waves of $[Ru_3^{II,III,III}(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_2(CO)]$.".

The text "and found that the π-type interaction of the CN^- ligand is of π-donor rather than π-acceptor (back-donation) type to the d^5- and d^6-based structural unit. This is due to the π-deficiency of the dimeric unit that uses the relevant d electrons for the formation of the "$Ru(d\pi)-O(p\pi)$ π-conjugated system." has been changed to "and found that the π-back-donation is less favorable. This is due to the poor π-donor properties of the dimeric unit as a result of usage of the relevant d electrons for the formation of the $Ru(d\pi)-O(p\pi)$ π-conjugated system.".

Page B (to be updated before publication). The text "Cyanide ion is known as a weaker π-acceptor and a stronger π-donor in comparison with CO." has been changed to "Cyanide ion is known as a weaker π-acceptor in comparison with CO.".

The following text has been deleted: "In this work, we found that CN^- in fact acts as a π-donor to the triruthenium unit, as in the case of the diruthenium core, $Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$.[48]"

In Table 1, the text "(4400),," has been changed to "(4400),".

The text "is ascribed to the π-donation of the cyano ligand that could cause a stronger $d\pi(Ru)-p\pi(\mu\text{-}O)$ interaction within the Ru_3O core to give" has been changed to "is ascribed to a stronger $d\pi(Ru)-p\pi(\mu\text{-}O)$ interaction within the Ru_3O core to give".

Page C (to be updated before publication). The text "significantly more than those of the corresponding py complex." has been changed to "significantly more than those of the corresponding py complex. This is, in part, due to the negative charge of the cyano ligand.".

The text "ligand coordinated to π-deficient $Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$ and $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6$ (vide infra) cores is more favorable for π-donation, at least in less acidic solvents." has been changed to "ligands coordinated to poor π-donating $Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$ and $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6$ (vide infra) cores are less favorable for π-back-donation.".

The text "As mentioned in the Introduction, the diruthenium unit $Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$, despite the involvement of electron-rich Ru(II) and Ru(III) centers," has been changed to "The diruthenium unit $Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$, despite the involvement of electron-rich Ru(II) and Ru(III) centers,".

The following text has been deleted: "This fact has been explained by considering the π-donating behavior of the cyanide ligand."

The text "$Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6$ core,[23] π-donation by the cyano ligand is also likely to operate for **1**." has been changed to $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6$ core,[23] π-back-donation to the cyano ligand in **1** could be weaker than that normally expected for the M(II)−CN linkage in typical transition-metal−cyano complexes.".

The following text has been deleted: "In fact, appreciable negative shifts of the redox potentials (for the $Ru_3^{II,II,III}/Ru_3^{II,III,III}$ and $Ru_3^{II,III,III}/Ru_3^{III,III,III}$ processes) of **1** measured in the less acidic CH_2Cl_2 support the operation of the π-donation of the cyano ligand in addition to the σ-donation in **1**."

Page D (to be updated before publication). The text "It is interesting to note that a red shift of 39 cm^{-1} for the CN ligand was observed when $Ru_3^{III,III,III}$ (2111 cm^{-1}) was reduced to $Ru_3^{II,III,III}$ (2072 cm^{-1}) while a blue shift (54 cm^{-1}) was found for the oxidation of $Ru_3^{III,III,III}$ (2111 cm^{-1}) to $Ru_3^{III,III,IV}$ (2165 cm^{-1}). The smaller wavenumber change of the $Ru_3^{II,III,III}/$

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$Ru_3^{III,III,III}$ process (39 cm^{-1}) than that of $Ru_3^{III,III,III}/Ru_3^{III,III,IV}$ (54 cm^{-1}) revealed two points: (i) in the $Ru_3^{II,III,III}/Ru_3^{III,III,III}$ process, the oxidation reaction did not occur on the CN-coordinated ruthenium, which indicated that the $Ru_3^{II,III,III}$ oxidation state of **1** was delocalized and no divalent charge was located on the CN-coordinated ruthenium. (ii) In the $Ru_3^{III,III,III}/Ru_3^{III,III,IV}$ process, the oxidation took place on the CN-coordinated ruthenium, through which the Ru_3O core received both σ- and π-donation from the cyanide ligand. Furthermore, the IR peak for the $Ru_3^{III,III,IV}$ seems to be wider than that of $Ru_3^{III,III,III}$ and $Ru_3^{II,III,III}$. This may indicate the lesser extent of delocalization in the $Ru_3^{III,III,IV}$ state with possibly somewhat positive charge in the CN-bound Ru." has been changed to "The red shift of 39 cm^{-1} for the CN ligand was observed when $Ru_3^{III,III,III}$ (2111 cm^{-1}) was reduced to $Ru_3^{II,III,III}$ (2072 cm^{-1}) while a blue shift (54 cm^{-1}) was found for the oxidation of $Ru_3^{III,III,III}$ (2111 cm^{-1}) to $Ru_3^{III,III,IV}$ (2165 cm^{-1}). The smaller change in the wavenumber of the $Ru_3^{II,III,III}/Ru_3^{III,III,III}$ process (39 cm^{-1}) than that of $Ru_3^{III,III,III}/Ru_3^{III,III,IV}$ (54 cm^{-1}) may reveal two points: (i) In the $Ru_3^{II,III,III}/Ru_3^{III,III,III}$ process, the oxidation reaction did not occur on the CN-coordinated ruthenium, which indicated that the $Ru_3^{II,III,III}$ oxidation state of **1** was delocalized and no divalent charge was located on the CN-coordinated ruthenium. (ii) In the $Ru_3^{III,III,III}/Ru_3^{III,III,IV}$ process, the oxidation took place on the CN-coordinated ruthenium.".

The text "While CN^- acts as a π-donor to the π-deficient core, CO receives a π-electron by π-back-donation, specifically in the oxidation state $Ru_3^{II,III,III}$." has been changed to "While CO acts as a strong π-acceptor to the triruthenium core specifically in the oxidation state $Ru_3^{II,III,III}$, CN^- does not.".

Page E (to be updated before publication). The text "charge of the CO-coordinated Ru is favorable for the back-donation to CO. In contrast," has been changed to "charge of the CO-coordinated Ru is favorable for the back-donation to CO. The structural localization of the CO complex indicates that the delocalized oxo-centered triruthenium core is not a good π-donor and requires the localization when a strongly π-accepting ligand coordinates. In contrast,".

The text "Therefore, the back-donation is unfavorable for the cyano complexes. The π-deficient nature of the $Ru_3(\mu_3\text{-}O)$ core requires the π-donation of CN^- to stabilize the dπ−pπ system of the core. Another example is $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(bpy)_2(CN)_2]$,[48] which is also characterized by a similar dπ(Ru)−pπ(O) interaction making the Ru_2O core π-deficient." has been changed to "Therefore, the back-donation in this direction is less favorable. The π-back-donations in the direction perpendicular to the Ru_3O plane may be operative but are unlikely to be significant if they occur. Structural localization would take place, if the cyano ligand required the strong π-back-donation.".

The following text has been deleted: "One example is the octahedral $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core,[59,60] which is considered to be π-defcient as a result of the metal−metal bond formation by using dπ electrons. While the cyano ligand could act as a π-donor to the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core core,[59] the CO complex can be stabilized by a high percentage of participation of the Se orbitals that was thought to be invoked for the cluster to CO back-donation.[60]"

The text "involved in the dπ−pπ interaction. The small contribution of CN^- (3%) to the LUMO, together with the aforementioned negative charge on the ligand, supports the π-donation from the ligand to the empty dπ−pπ orbital." has been changed to "involved in the dπ−pπ interaction.".

Page F (to be updated before publication). The text "stabilization of the $Ru_3^{II,III,III}$ state against oxidation, but the π-donation from the CN^- ligand also makes a contribution, as indicated previously for the diruthenium complex $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(bpy)_2(CN)_2]$.[48]" has been changed to "destabilization of the $Ru_3^{III,III,III}$ state against oxidation.".

The text "The CN^- ligand acts as a π-donor as well as a σ-donor, as evidenced by the negative shift of the redox potentials of the processes $Ru_3^{II,II,III}/Ru_3^{II,III,III}$ and $Ru_3^{II,III,III}/Ru_3^{III,III,III}$, in comparison with those of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$." has been changed to "The negative shift of the redox potentials of the processes $Ru_3^{II,II,III}/Ru_3^{II,III,III}$ and $Ru_3^{II,III,III}/Ru_3^{III,III,III}$, in comparison with those of $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(py)_3]^+$, is partly explained in terms of the negative charge.".

The text "It was suggested that the triruthenium core is basically π-electron deficient, as the π-electrons are used for the formation of the (Ru)dπ−(μ-O)pπ π-conjugated system. The poor π-donor ligand CO is stabilized by the charge localization of the core in the $Ru_3^{II,III,III}$ state, where the divalent state is localized to the CO-bonded Ru. The difference in the role of two ligands is further discussed with the aid of MO calculations to support the π-donating behavior of the CN^- ligand. Further investigation on the coordination behavior of the cyanide ligand to other metal clusters with metal−metal bonding interactions or dπ−pπ interactions is certainly of interest." has been changed to "The difference has been interpreted in terms of the different π-acceptor properties of the two ligands when they coordinate to the mixed-valent $Ru_3^{II,III,III}$ core. The strong π-accepting ligand CO is stabilized by the charge localization of the core in the $Ru_3^{II,III,III}$ state, where the divalent state is localized to the CO-bonded Ru. In contrast, the triruthenium core shows a delocalized structure in the cyano complex. The difference in the role of two ligands is further discussed with the aid of MO calculations. Further comparative studies on the coordination behavior of the two ligands to other metal clusters with metal-metal bonding interactions or dπ−pπ interactions are certainly of interest.".

The text "B3LYP function by using the Gaussian 03 program.[61]" has been changed to "B3LYP function by using the Gaussian 03 program.[59]".

The text "referenced to the crystal structure of $[Ru_3^{II,III,III}(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(py)_3]$.[62]" has been changed to "referenced to the crystal structure of $[Ru_3^{II,III,III}(\mu_3\text{-}O)(\mu\text{-}CH_3CO_2)_6(py)_3]$.[60]".

Page H (to be updated before publication). The following text has been deleted: "(59) Yoshimura, T.; Ishizaka, S.; Sasaki, Y.; Kim, H. B.; Kitamura, N.; Naumov, N. G.; Sokolov, M. N.; Fedorov, V. E. *Chem. Lett.* **1999**, 1121−1122. (60) (a) Orto, P. J.; Nichol, G. S.; Okumura, N.; Evans, D. H.; Arratia-Perez, R.; Ramirez-Tagle, R.; Wang, R.; Zheng, Z. *Dalton Trans.* **2008**, 4247−4253. (b) Orto, P. J.; Nichol, G. S.; Wang, R.; Zheng, Z. *Inorg. Chem.* **2007**, *46*, 8436−8438."

The text "(61) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.;" has been changed to "(59) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.;".

The text "(62) Marr, S. B.; Carvel, R. O.; Richens, D. T.; Lee, H. J.; Lane, M.;" has been changed to "(60) Marr, S. B.; Carvel, R. O.; Richens, D. T.; Lee, H. J.; Lane, M.;"

The Supporting Information file has been replaced.