

Bis(2,4-pentanedionato)cobalt(II)

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The structure of $\text{Co}(\text{acac})_2$ reported by us [Burgess *et al.* (2000). *Acta Cryst.* **C56**, 649–650] has been reassessed in view of a recent article [Vreshch *et al.* (2010). *Inorg. Chem.* **49**, 8430–8434], which suggests that the compound might actually be $\text{Cu}(\text{acac})_2$. Using the structure-factor data deposited with the original article, the evidence is slightly in favour of $\text{Cu}(\text{acac})_2$, although the crystallographic data alone, in this case, cannot unequivocally distinguish between the two possibilities. We concede that we may indeed have been mistaken, but that there is still some element of mystery.

Comment

Under the title ‘Monomeric Square-Planar Cobalt(II) Acetylacetonate: Mystery or Mistake’, Dikarev and co-workers (Vreshch *et al.*, 2010) have recently challenged our determination of the structure of the title compound (Burgess *et al.*, 2000). We were at the time surprised at our isolation of unsolvated monomeric bis(2,4-pentanedionato)cobalt(II) [cobalt(II) acetylacetonate], for four of the five reasons listed in their *Introduction*. We do not share their surprise at our product being green [$\text{Cu}(\text{acac})_2$, which they deem our product to be, is blue]. Indeed we consider any attempt to use colour as diagnostic or predictive of stereochemistry for transition metal complexes to be unwise. Octahedral cobalt(II) complexes, though often pink, can be any shade of the six primary and secondary colours, including the deep blue commonly assumed diagnostic of tetrahedral cobalt(II) species (Bartecki *et al.*, 2011). Moreover, in view of the big difference between the ‘typical’ colours of pink for octahedral, blue for tetrahedral Co^{2+} complexes, how is one to predict with any confidence the ‘expected’ colour of square-planar Co^{2+} species?

Thanks to a detailed re-examination of our X-ray data, very kindly undertaken by the Editor of *Acta Cryst. Section C* (Linden, 2011), it is apparent that our data may be interpreted in terms of $\text{Co}(\text{acac})_2$ or $\text{Cu}(\text{acac})_2$, though admittedly the evidence is just slightly in favour of the latter. The structure-factor data deposited with the original article were used in a re-refinement of the original model in which the Co atom was replaced by a Cu atom. The *R* factor reduced from 0.0515 (for Co) to 0.0508 (for Cu), which is hardly significant. Plots of contoured difference Fourier map sections passing through the metal centre are quite noisy and they show no discernable differences between the two refinements, although the maximum and minimum residual electron-density values are actually larger for the Cu refinement (0.98 and $-1.11 \text{ e } \text{Å}^{-3}$, respectively, for the Co model compared with 1.14 and $-1.28 \text{ e } \text{Å}^{-3}$ for the Cu model). Validation of the Co model reveals a *C alert* for the Hirshfeld test involving the Co1–O1 and Co1–O2 bonds. This test is sometimes indicative of misassigned elements in the model (Hirshfeld, 1976; Spek, 2009). There is no corresponding validation alert with the Cu model. In view of this, and of the chemical reasons to be suspicious of the nature of our product, there is a real possibility that our original publication is in error. Unfortunately, none of the original four authors now has access to either the laboratory or computational facilities needed to attempt to repeat our work. The answer to the question posed by the title of our critics’ paper is thus that we may indeed have been mistaken, but that there is still some element of mystery. We may even have had a mixed or doped product $(\text{Co,Cu})(\text{acac})_2$; contamination of the Co material by a little Cu may well have templated the Co molecule, thus leading to the unusual geometry for the Co complex. Curiously the *R* factor in the above test refinements drops to 0.0493 if a 1:1 Co:Cu mixture is assumed. In any event, we do not subscribe to the philosophy that unexpected products cannot be made [*cf.* inert gas compounds and Dasent (1965)].

References

- Bartecki, A., Burgess, J. & Kurzak, K. (2011). *The Color of Metal Compounds*, 3rd ed., ch. 4. Boca Raton, Florida, USA: Taylor and Francis.
- Burgess, J., Fawcett, J., Russell, D. R. & Gilani, S. R. (2000). *Acta Cryst.* **C56**, 649–650.
- Dasent, W. E. (1965). In *Nonexistent Compounds*. New York: Marcel Dekker.
- Hirshfeld, F. L. (1976). *Acta Cryst.* **A32**, 239–244.
- Linden, A. (2011). Private communication.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Vreshch, V. D., Yang, J.-H., Zhang, H., Filatov, A. S. & Dikarev, E. V. (2010). *Inorg. Chem.* **49**, 8430–8434.