Relationship of *cis*-Diammineplatinum α-Pyridone Blue to Other Platinum Blues. An X-Ray Photoelectron Study

J. K. Barton,[1a] S. A. Best,[1b] S. J. Lippard,*[1a] and R. A. Walton*[1b]

Contribution from the Departments of Chemistry, Purdue University, West Lafayette, Indiana 47907, and Columbia University, New York, New York 10027. Received November 14, 1977

Abstract: The x-ray photoelectron spectrum (XPS) of crystalline *cis*-diammineplatinum α-pyridone blue, [Pt$_2$(NH$_3$)$_4$-(C$_5$H$_4$ON)$_2$]$_2$(NO$_3$)$_5$, has been investigated and the Pt 4f binding energies of this complex found to be similar to those exhibited by Pt(II) complexes such as *cis*-(H$_3$N)$_2$PtCl$_2$. This result is in accord with the previous assignment of a formal platinum oxidation state of 2.25 in the blue α-pyridone complex. The widths of the Pt 4f peaks (fwhm ~1.3) indicate that the binding energies associated with the two geometrically different types of Pt environments in the α-pyridone oligomer are very similar, the implication being that within the Pt$_4$ unit there must be a considerable delocalization of charge. A comparison of the XPS data for the α-pyridone blue with that found for the platinum uracil and acetamide blues shows that these species have similar electronic structures, there being no evidence that they are pure derivatives of Pt(IV). The XPS of some samples of the acetamide blue ("Platinblau") show the presence of small amounts of higher oxidation state contaminants, consistent with the difficulty in preparing this species in a reproducibly pure form. The Pt(III) dimer K$_2$Pt$_2$(SO$_4$)$_4$·3H$_2$O possesses Pt 4f binding energies which are much closer to those of coordination complexes of Pt(IV) than Pt(II).

Introduction

Hydrolysis of the acetonitrile complex of divalent platinum, *cis*-PtCl$_2$(NCCH$_3$)$_2$, in the presence of silver salts produces a blue product first designated as "Platinblau".[2] This material was previously thought to have the composition Pt^{II}-(CH$_3$CONH)$_2$·H$_2$O,[2,3] but more recently has been reformulated[4] as the platinum(IV) species Pt^{IV}(CH$_3$CONH)$_2$-(OH)$_2$ on the basis of detailed studies made of a related trimethylacetamide system. Within the last year, a kinetic study of the hydrolysis of acetonitrile coordinated to platinum(II) supported the idea that "Platinblau" should be formulated as an acetamidato derivative of platinum(IV).[5]

A second major class of platinum blues arise from the reaction between the aquated products[6] of *cis*-dichlorodiammineplatinum(II) (DDP) and polyuracil, uracil, 1-methyluracil, uridine, thymine, and other, related pyrimidines.[7,8] The discovery that the platinum pyrimidine blues, like DDP itself, exhibit antitumor activity[7,9] has provided added impetus to the study of these intriguing species.

A breakthrough in the structural and electronic characterization of the platinum blues was the recent isolation[10] of a crystalline blue platinum complex from the reaction of *cis*-[(NH$_3$)$_2$Pt(OH$_2$)$_2$]$^{2+}$ with α-pyridone (**1**). The resulting

α-pyridone (**1**)
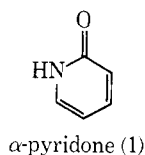
compound, [Pt$_2$(NH$_3$)$_4$(C$_5$H$_4$ON)$_2$]$_2$(NO$_3$)$_5$, has a bridged oligomeric structure (see Figure 1) involving partially oxidized platinum atoms of average formal oxidation state 2.25.

A fundamental question concerns the relationship between *cis*-diammineplatinum α-pyridone blue and the other amide-containing blues. This comparison is difficult because the latter are amorphous compounds. In order to learn whether the α-pyridone blue embodies features exhibited by the other blues, we have investigated the x-ray photoelectron spectra (XPS) of [Pt$_2$(NH$_3$)$_4$(C$_5$H$_4$ON)$_2$]$_2$(NO$_3$)$_5$ and other platinum blues. This technique is appropriate for the characterization of both crystalline and amorphous phases.[11] The present report provides the details of this XPS study.

Experimental Section

Preparation and Characterization of the Platinum Blues. *cis*-Di-

ammineplatinum α-Pyridone Blue. A 0.15 M solution of *cis*-diammineplatinum(II) hydrolysis products was prepared by mixing 0.3 g of *cis*-(NH$_3$)$_2$PtCl$_2$ and 0.34 g of AgNO$_3$ in approximately 7 mL of water. After being stirred in the dark at room temperature overnight, the solution was centrifuged twice to remove the AgCl precipitate. One equivalent of α-pyridone (2-hydroxypyridine) dissolved in a minimum amount of water and adjusted to pH >10 with 0.1 N NaOH was then added to the *cis*-diamminediaquoplatinum(II) solution and the reaction mixture was adjusted to neutral pH with 0.1 N NaOH. The solution was then incubated in the dark at 37–40 °C for approximately 24 h until a deep blue-green color appeared in the solution. Following incubation, a few drops of concentrated nitric acid and 0.75 g of sodium nitrate were added to the blue-green solution, pH ~1. The solution immediately turned very dark blue in color and was allowed to stand for 12 h at 0 °C. Dark blue needles were collected. Analytical data were reported previously.[10]

cis-Diammineplatinum Uracil Blue. The uracil derivative was prepared by incubation at 37 °C of a mixture of *cis*-diammineplatinum(II) hydrolysis products (0.15 M) to which was added a concentrated basic (pH >10) solution containing 1 equiv of uracil. Subsequent steps were carried out as described for the α-pyridone blue. Following formation of a blue-green color in solution (approximately 24 h), a blue powder could be precipitated with an equal volume of ethanol and an excess of cold ether. Anal. Calcd for Pt(C$_4$N$_2$H$_3$O$_2$)-(NH$_3$)$_2$(NO$_3$)$_{1.25}$(H$_2$O): C, 11.03; H, 2.54; N, 16.88; Pt, 44.77; O, 24.78. Found: C, 11.20; H, 2.56; N, 14.18; Pt, 46.02; O, 25.92.

Platinum Acetamide Blue. (1) Procedure A. A sample of 0.167 g of K$_2$PtCl$_4$ was dissolved in 25 mL of 0.1 N aqueous acetonitrile and heated to 65 °C for approximately 18 h. Following the formation of a deep blue color in solution, 4 equiv of AgNO$_3$ was added, and the mixture was allowed to stir in the dark overnight. After several centrifugations to remove silver chloride, the deep blue solution was evaporated to a volume of approximately 5 mL under reduced pressure. A dark blue powder was collected by precipitation with ethanol and ether, redissolved in water, and reprecipitated with these solvents. This procedure was repeated several times. The XPS of the first sample prepared by this method (no. 1 in Table I) revealed contamination with nitrate salts. Accordingly, the two other samples (no. 2 and 3) were further purified by eluting a methanol solution of the complex through an alumina column followed by ether precipitation.

(2) Procedure B. The second set of acetamide blue samples (no. 4 and 5) was prepared according to the original method[2] and purified by chromatography as suggested in ref 4.

Preparation and Characterization of the Platinum(III) Dimer K$_2$Pt$_2$(SO$_4$)$_4$·3H$_2$O. This complex was obtained as described in the literature.[12] Its infrared spectrum and microanalyses were in agreement with those reported.[12] Anal. Calcd for K$_2$Pt$_2$(SO$_4$)$_4$(H$_2$O)$_3$: H, 0.67; Pt, 43.03; S, 14.14. Found: H, 0.57; Pt, 43.40; S, 13.87.

Spectral Measurements. X-ray photoelectron spectra were recorded using a Hewlett-Packard Model 5950A ESCA spectrometer.

Table I. Core Electron Binding Energies of Various Platinum Blues[a]

Compd	Sample no.[b]	Pt 4f		N 1s		O 1s	C 1s	
		5/2	7/2	Ligand	NO_3^-			
α-Pyridone blue	1	76.2 (1.2)[c,d]	72.8 (1.2)[c,d]	400.0 (1.5)	406.3 (1.3)	531.9	284.5	287.1[e]
	2	76.2 (1.5)	72.8 (1.4)	399.9 (1.6)	406.4 (1.2)	531.9	284.7	~287.0[e]
	3	76.3 (1.3)	73.0 (1.2)	400.1 (1.5)	406.4 (1.5)	532.0	284.8	~287.0[e]
Uracil blue	1	76.3 (1.6)	73.0 (1.6)	400.2 (1.8)	~406.6[e]	531.8	~284.8	288.2
	2	76.0 (1.6)	72.7 (1.5)	399.8 (1.9)	406.1[e]	531.7	284.5	~287.9[e]
	3	76.1 (1.6)	72.7 (1.5)	399.7 (2.2)	406.3[e]	531.5	284.7	287.6[e]
Acetamide blue	1	76.2 (1.7)[c]	73.0 (1.7)[c]	398.7 (1.7)	406.3 (1.6)	531.8	284.6	287.0
	2	76.1 (1.6)[c]	72.9 (1.6)[c]	399.0 (2.0)		531.7	285.0	~287.2[e]
	3	76.0 (1.8)[c]	72.8 (1.8)[c]	398.9 (2.1)		531.8	284.8	287.4
	4	75.8 (2.0)	72.6 (2.0)	398.8 (2.2)		531.7	285.1	287.2[e]
	5	75.8 (2.0)	72.6 (1.8)	398.9 (2.2)		531.8	284.9	~287.0[e]

[a] Binding energies (eV) are accurate to ±0.1 eV except for certain of the C 1s which are ±0.2 eV; fwhm values are given in parentheses. [b] Different preparative samples. [c] Fwhm value determined by a deconvolution procedure (see text). [d] Higher energy doublet located at 77.4 and 74.2 eV. [e] Weak, broad peak.
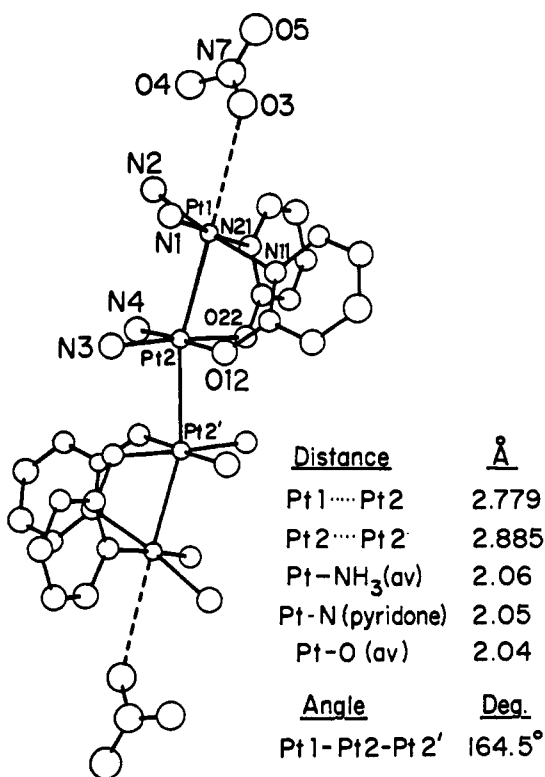

Distance	Å
Pt 1····Pt 2	2.779
Pt 2····Pt 2⁻	2.885
Pt-NH₃(av)	2.06
Pt-N (pyridone)	2.05
Pt-O (av)	2.04

Angle	Deg.
Pt 1-Pt 2-Pt 2'	164.5°

Figure 1. Structure[10] of *cis*-diammineplatinum α-pyridone blue, [Pt₂(NH₃)₄(C₅H₄ON)₂]₂(NO₃)₅.

Monochromatic aluminum Kα₁,₂ radiation (1486.6 eV) was used as the x-ray excitation source and the powdered samples were dispersed on a gold-plated copper surface. Under these conditions, the carbon 1s binding energy of graphite is close to 284.0 eV. As before,[13,14] this binding energy was used regularly to monitor the performance of the instrument. During the period when the spectra of the platinum complexes were recorded, this C 1s peak had a full width at half maximum (fwhm) value of 0.85 ± 0.15 eV. The spectrometer was used with an electron "floodgun" in operation, a procedure that eliminates, or at least reduces to a minimum, surface charging effects.[14] The measured binding energies were standardized using a Au 4f₇/₂ binding energy of 83.8 eV.[15] Deconvolutions were carried out using a Du Pont 310 curve resolver according to a previously described procedure.[13]

Results and Discussion

***cis*-Diammineplatinum α-Pyridone Blue.** The α-pyridone complex [Pt₂(NH₃)₄(C₅H₄ON)₂]₂(NO₃)₅ affords the opportunity to obtain the core electron binding energies of a

structurally characterized platinum blue. Table I summarizes binding energy data for three different preparative samples of this complex. A typical Pt 4f spectrum of the α-pyridone blue appears in Figure 2 (spectrum A). For each preparative sample the binding energies and peak shapes showed no time dependence. The N 1s, O 1s, and C 1s binding energies are normal.[16,17] A comparison of these data with the N 1s, O 1s, and C 1s binding energies of the free ligands provides little useful structural information with the exception of the identification of the N 1s binding energies arising from the presence of NO_3^-.

The Pt 4f binding energies of the α-pyridone blue are very similar to those of the Pt(II) complex *cis*-(H₃N)₂PtCl₂, the spectrum of which was recorded immediately after that of the blue. This complex has Pt 4f₅/₂,₇/₂ binding energies at 76.1 and 72.8 eV and these peaks possess fwhm values (1.3 eV) which were identical with those of the α-pyridone blue. From data obtained on *cis*-(H₃N)₂PtCl₂ and *cis*-(H₃N)₂PtCl₄ and that of other workers[18-22] for additional pairs of Pt(II)-Pt(IV) complexes, it is clear that the Pt 4f binding energies of Pt(IV) species are between 2 and 3 eV higher than those of their Pt(II) analogues.[23] In the case of *cis*-(H₃N)₂PtCl₄, the Pt 4f₅/₂,₇/₂ binding energies are at 78.7 and 75.4 eV (fwhm = 1.3 eV), higher by ~2.5 eV than those of (H₃N)₂PtCl₂ and the α-pyridone blue.

The crystal structure determination of the α-pyridone blue reveals two sets of Pt environments. Nonetheless, there is no evidence for two sets of Pt 4f binding energies. This observation is consistent with delocalization of charge within this paramagnetic cation where the average formal oxidation state of the platinum atoms is 2.25. The resultant charge at each Pt center is therefore not much different from that present in Pt(II) complexes such as (H₃N)₂PtCl₂.

One initially unexpected feature of the XPS of the first α-pyridone blue sample to be studied was the appearance of an additional Pt 4f₅/₂,₇/₂ doublet located at ~1.5 eV to the high binding energy side of the Pt 4f peaks of the pure compound. This result, shown in Figure 2 (spectrum B), was obtained for preparative sample no. 1 listed in Table I. The origin of the two sets of Pt 4f₅/₂,₇/₂ doublets in this sample was initially thought to be the two different Pt environments in the complex, an assignment consistent with the known structure (see above). The chemical shift of +1.5 eV seemed unexpectedly large, however, and upon deconvoluting this spectrum (Figure 2B), unacceptably large fwhm values (2.1 eV vs. the 1.2 eV for the lower energy doublet) had to be given the higher energy Pt 4f₅/₂,₇/₂ set in order to arrive at a 1:1 stoichiometric ratio for the two types of platinum signals. An alternative explanation was that the higher energy set of peaks arose from "shake-up"

or some related phenomenon, a remote possibility in view of the rare occurrence of shake-up satellite peaks in the XPS of second- and third-row transition metal complexes.[24] Since this higher energy set of Pt $4f_{5/2,7/2}$ peaks was not observed in the XPS of any other preparative samples of the α-pyridone blue (see Table I and Figure 2A), however, it is due to a contaminant, probably arising from some higher oxidation state platinum species. Formally higher oxidation state platinum species have been isolated from the reaction medium which affords $[Pt_2(NH_3)_4(C_5H_4ON)_2]_2(NO_3)_5$.[10] It is possible that the oxidation state of such a "contaminant" may be closer to Pt(+3) than Pt(+2) since we find that the Pt $4f_{5/2,7/2}$ binding energies of the platinum(III) dimer $K_2Pt_2(SO_4)_4\cdot3H_2O$[12] are 78.5 and 75.2 eV (fwhm values of 1.4 eV).[25] The present results demonstrate the value of XPS to check the purity of platinum blues which are notoriously difficult to prepare reproducibly pure.

Acetamide and Uracil Blues. The related acetamide and uracil blues exhibit Pt 4f binding energies that are very similar to those of the α-pyridone blue (Table I). Accordingly, the XPS evidence favors the assignment of formal oxidation state close to +2 for these materials, and casts strong doubt upon the formulation[4,5] of "Platinblau" as $Pt^{IV}(CH_3CONH)_2(OH)_2$. The present data are in excellent agreement with the only other results of an XPS study on platinum blues. This study[20] is largely concerned with the trimethylamide platinum blue. The Pt 4f binding energies of original samples of the three components found to occur in the apparently homogeneous crystals of the trimethylacetamide analogue of "Platinblau"[4] were measured.[20] In all instances, the Pt $4f_{7/2}$ energies (73.1-73.4 eV) clearly showed[20] the absence of Pt(IV) species in good agreement with the binding energies found here to be characteristic of the α-pyridone blue. Attempts[20] to prepare these same trimethylamide phases using the published method[4] gave two blue phases and not the two yellow and one blue phase originally described.[4] Once again, however, the Pt $4f_{7/2}$ energies reported (73.4 eV)[20] are close to those measured here (Table I), although one difference between the two studies is the greater reported[20] peak widths for the Pt $4f_{7/2}$ lines (2.2 eV) than generally observed in the present work (see Table I).

A variety of pyrimidine blues had previously been formulated[7] as "Pt(pyrimidine)(NH₃)₂(OH)₃", based on elemental analyses. The XPS of *cis*-diammineplatinum uracil blue, however, reveals N 1s peaks characteristic of nitrate anions. Since the synthesis of the pyrimidine blues requires the use of silver nitrate, the extra oxygen atoms in the analyses probably arise from the presence of nitrate anions. The high oxygen content does not require one to postulate a Pt(IV) oxidation state. The pyrimidine blues may instead be formulated as $[Pt(pyrimidine)(NH_3)_2(NO_3)_{1.25}]$ by analogy to the α-pyridone blue. Variability in the chemical analyses could result both from the presence of contaminants containing fewer ammine ligands[26] and from differences in the degree of hydration of the complex.

The quality of the Pt 4f binding energy spectra obtained for the different samples of the uracil blues was comparable to that of the fully characterized α-pyridone blue. The uracil blue peaks were only slightly broader (fwhm ~1.5 eV) than those of the α-pyridone system and there was no evidence for any significant amount of contamination by higher oxidation state platinum species (see Figure 2C).

Study of the XPS of the acetamide blues is more complex than that of the related α-pyridone or uracil blues since they are more difficult to prepare in reproducibility pure form. The Pt 4f peaks of the acetamide blues prepared by procedure A (no. 1-3 in Table I) were asymmetric owing to a contribution from a low-intensity Pt $4f_{5/2,7/2}$ doublet located at ~+1.5 eV relative to the main Pt 4f peaks. This feature is reminiscent of
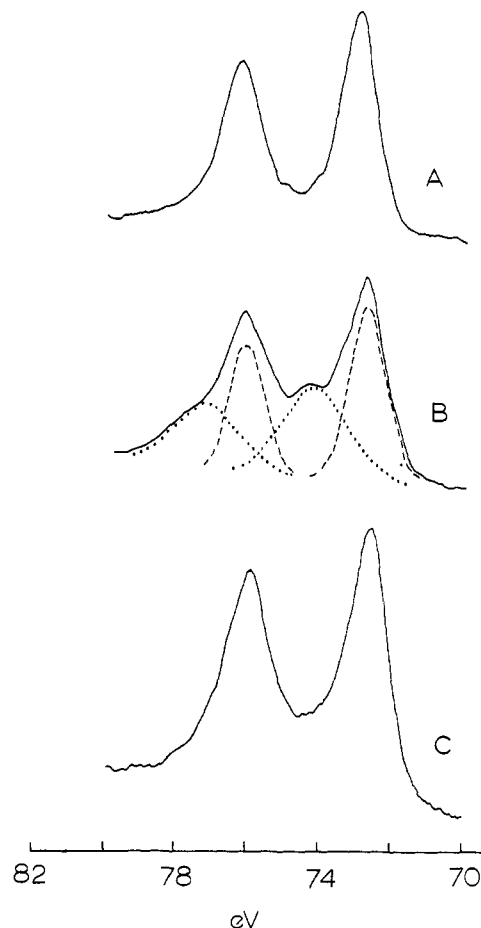

Figure 2. Pt 4f binding energy spectra of (A) pure *cis*-diammineplatinum α-pyridone blue, (B) a sample of platinum α-pyridone blue containing a high Pt 4f binding energy contaminant, and (C) platinum uracil blue. Spectrum B has been deconvoluted into two sets of Pt 4f doublets using the parameters $\Delta E(4f_{5/2} - 4f_{7/2}) = 3.3 \pm 0.1$ eV and $I(4f_{7/2})/I(4f_{5/2}) = 4/3$ for the individual sets of $4f_{5/2,7/2}$ doublets and fwhm values of 1.3 $\pm$ 0.1 eV for the lowest energy $4f_{5/2,7/2}$ doublet.

that arising from the contamination present in one of the samples of the α-pyridone blue (no. 1 in Table I) attributed to a higher oxidation state platinum species. All three samples (no. 1-3) were found to contain Ag(I),[27] characterized by Ag $3d_{3/2,5/2}$ binding energies at 374.0 and 368.0 eV, which originate from the $AgNO_3$ used in their synthesis. Furthermore, sample no. 1, which was not subjected to a final purification step (elution through an alumina column), was found to contain nitrate ion (see Table I), a contaminant which is not present in the more highly purified samples 2 and 3. In view of the considerable difficulty experienced in preparing pure samples of the various acetamide blues,[2,3] our observations are consistent with these materials being mixtures, the major component of which bears a close electronic resemblance to *cis*-diammineplatinum α-pyridone blue.

In an effort to circumvent the problems associated with impure acetamide blues, two samples (no. 4 and 5 in Table I) were prepared by the alternative procedure B, employing the method[4] in which purification is carried out using column chromatography. The resulting acetamide blues have Pt 4f binding energies which are the same as those of the other blues listed in Table I. While these peaks are slightly broader than those associated with the α-pyridone and uracil blues, they no longer possess the asymmetry which is characteristic of the other samples of the acetamide blues (no. 1-3). In addition, these products are now free from Ag^+ and NO_3^- contaminants.

Conclusion

The XPS of the three classes of platinum blues examined in this study clearly demonstrate that they have similar electronic structures. An independent investigation[28] of *cis*-diammineplatinum uridine blue by EXAFS spectroscopy showed it to have a geometry consistent with that found for the α-pyridone blue. It therefore appears that, as stated previously,[10] the features embodied in *cis*-diammineplatinum α-pyridone blue, namely, a mixed oxidation state, amidate bridged, oligomeric structure, are reflective of the entire class of "Platinblau" compounds.

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Molecular and Electronic Structure of Tetraallyldirhenium

F. Albert Cotton* and Michael W. Extine

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. Received November 16, 1977

Abstract: The title compound, whose preparation was recently reported by Wilkinson and co-workers, has been investigated to determine its molecular structure and to clarify the nature of the multiple Re–Re bond. The structure is quite different from that of the Cr and Mo compounds of the same stoichiometry. The $Re_2(C_3H_5)_4$ molecule has virtual D_{2h} symmetry and no bridging allyl groups. The mean Re–Re distance in the two crystallographically independent molecules is 2.225 (7) Å. The four chemically equivalent $Re(\eta^3-C_3H_5)$ bonds are typical of metal to η^3-allyl bonds in general. The electronic structure has been treated using the Hartree–Fock–Roothaan SCF method in the Fenske–Hall approximation. The highest filled orbital is of a_1 symmetry and has δ-antibonding character. However, electrons occupying it do not appear to destabilize the molecule very much. There are strong π and σ M–M bonds. The Re–Re bond can be considered effectively triple. The crystallographic data are: space group $C2$ with $a = 12.218$ (3), $b = 8.692$ (2), $c = 18.763$ (4) Å, $\beta = 97.28$ (2)°, $Z = 6$. There are four molecules on the general position and two on the special positions of type $(0,y,0; 1/2,1/2 + y, 0)$ having C_2 symmetry. The structures of the two crystallographic types of molecule are essentially identical.

Introduction

A number of recent observations have combined to focus attention on the question of how sensitive M–M bond lengths are to the gain or loss of δ or δ* electrons. The cleanest case available involving metal atoms in the second transition series is provided by the $Mo_2(SO_4)_4{}^{4-}$ and $Mo_2(SO_4)_4{}^{3-}$ ions, where the first one has a $\sigma^2\pi^4\delta^2$ configuration and the second a $\sigma^2\pi^4\delta$ configuration.[1] The corresponding Mo–Mo distance are 2.111 (1) and 2.164 (2) Å. This increase of ca. 0.05 Å upon the loss of one δ electron takes place with retention of essentially identical structural constraints.[2] Consistent with this is the fact that Mo–Mo triple bonds, where there are no δ electrons, have lengths in the range 2.16–2.22 Å.[3,4] Thus, each addition of a one-half δ component seems to shorten an Mo–Mo bond by roughly 0.05 Å.

In the third transition series, however, the evidence available at present, though limited, tends to imply that δ bonding has less of an effect on the bond length. Thus, in the $W_2(CH_3)_8{}^{4-}$ and $[W_2(CH_3)_{8-x}Cl_x]^{4-}$ ions[5] which have quadruple bonds, the W–W distances are about 2.26 Å while in the triply bonded