

related uranyl complex. Liquid–liquid extraction studies are in progress that will provide a quantitative evaluation of the separation capabilities of the ligands.

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Supplementary Material Available: Table SI, listing thermal parameters (2 pages); Table SII, listing observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139,
and Department of Radiology, Harvard Medical
School and Brigham and Women's Hospital,
Boston, Massachusetts 02115

⁹⁹Tc NMR Spectroscopy of Technetium(I) Phosphine and Phosphite Complexes

Alan Davison,^{*1a} James F. Kronauge,^{1a} Alun G. Jones,^{1b}
Ronald M. Pearlstein,^{1a} and John R. Thornback^{1a}

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The recent increased interest in the chemistry of technetium, due to its widespread use in nuclear medicine, has led us to investigate the use of ⁹⁹Tc NMR spectroscopy as a tool for the identification of technetium complexes. ⁹⁹Tc, which is obtained free from isotopic contamination, has a nuclear spin of 9/2 and a very high receptivity relative to ¹H of 0.275. The standard reference sample for this isotope is taken as (NH₄)[TcO₄] in D₂O which resonates² with $\delta = 22\,508\,304$. We have studied a range of diamagnetic complexes with technetium in the oxidation states +1 to +7, but in this brief note we wish to report some of our studies on technetium(I) complexes since it appears that erroneous data may have appeared recently.

Experimental Section

Caution! ⁹⁹Tc is a β^- emitter ($t_{1/2} = 2.1 \times 10^5$ years). All manipulations of solutions and solids were performed in a laboratory approved for the handling of radioisotopes using precautions outlined elsewhere.³

The complexes [Tc(dmpe)₃](PF₆)⁴ and [Tc(P(OMe)₃)₆](BPh₄)⁵ were prepared by literature methods. Ammonium pertechnetate was supplied as a gift by DuPont Biomedical Products.

⁹⁹Tc NMR spectra were recorded at 23 °C on a Varian XL-300 instrument with a 7.05-T superconducting magnet. A 34- μ s pulse width (90° tip) and 0.15-s acquisition time were used. No additional relaxation delay was used unless TcO₄⁻ ($T_1 = 0.1$ s)^{2,6} was present. The spectral width was set at 10⁵ Hz by using 30016 data points in the FID weighted with 10-Hz Gaussian line broadening. The reference sample ((NH₄)[⁹⁹TcO₄] in D₂O = 0 ppm) resonates at 67.516 MHz in this spectrometer. For differences greater than the maximum spectral width (10⁵ Hz, 1480 ppm) obtainable, chemical shifts could be calculated manually based on the spectrometer frequency, transmitter offset, transmitter base offset, and relative shift within the spectral window. We estimate that the error associated with these values is $\sim \pm 2$ ppm.

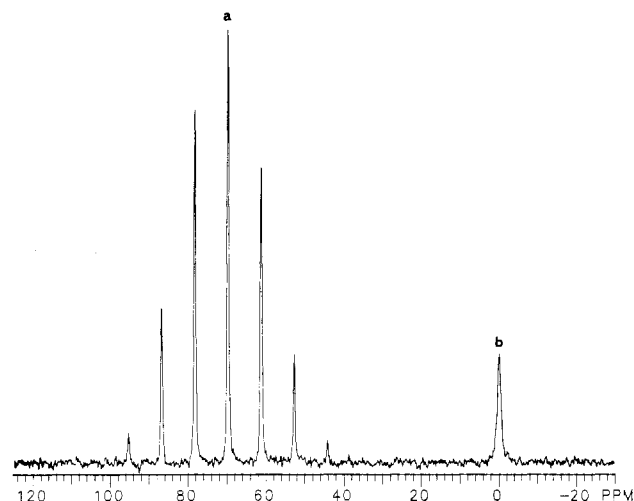


Figure 1. ⁹⁹Tc NMR spectrum of a mixed sample containing (a) [Tc(dmpe)₃](PF₆) and (b) [Tc(CNBU₆)₆](PF₆) in CDCl₃ showing the proximity of their chemical shifts. The chemical shift of [Tc(CNBU₆)₆]⁺ (-1914 ppm) is arbitrarily set to 0 ppm.

The absence of spectral folding or other artifacts was ruled out by changing the transmitter offset by a known frequency and verifying that the resonance moved within the spectral window by the appropriate amount and in the expected direction. For example, decreasing the transmitter offset by 10000 Hz should lead to a relative positive chemical shift of ~ 150 ppm.

Results and Discussion

The known chemical shifts for technetium complexes range from +2800 ppm for the *trans*-dioxotetrakis(pyridine)technetium(V) cation to -3672 ppm for the nonahydridotechnetate(VII) dianion, relative to that for ammonium pertechnetate(VII), 0 ppm. The former has been determined in our laboratory while the resonance of TcH₂²⁺ was reported by Lock,⁶ who also first measured the resonance of a Tc(I) complex, [Tc(CNBU₆)₆]⁺, at -1902 ppm. We have remeasured this compound with several different spectrometers and find its resonance in good agreement with that previously reported, coming at -1914 ppm. Spectra of more than 20 different analogues with substituted isocyanides have been measured, and all fall within ± 50 ppm of the *tert*-butyl derivative. Recently, Lorenz and co-workers⁷ have measured the resonances of Tc₂(CO)₁₀, a spin-paired Tc(0) species, and the Tc(I) carbonyl complexes Tc(CO)₅Br and TcCl(CO)₃(PPh₃)₂. The shift of the first is at -2477 ppm while those for the others occur at -1630 and -1488 ppm, respectively.

The basic spectral range may be readily understood in terms of the Griffith and Orgel theory,⁸ which relates chemical shifts to the ΔE between HOMO and LUMO. Our technetium study correlates well with the observations for ⁹⁵Mo NMR spectroscopy,⁹ in which MoO₄²⁻ appears near the center of the chemical shift range while Mo(CO)₆ is at -2000 ppm relative to the molybdate reference. The chemical shifts for molybdenum(0) complexes, -1000 to -2120 ppm, agree well with our observations for the isoelectronic technetium(I) species. Additionally, it is known that d² molybdenum(IV) species are heavily deshielded and the shifts occur at lower field than those for molybdate. Similarly, the technetium(V) species that we have studied have resonances downfield from pertechnetate.

We were surprised, therefore, that two other groups reported^{4,10} that the resonance of the technetium(I) complex [Tc(dmpe)₃]⁺ (dmpe = 1,2-bis(dimethylphosphino)ethane) occurred at -13 ppm

- (1) (a) Massachusetts Institute of Technology. (b) Harvard Medical School.
- (2) Buckingham, M. J.; Hawkes, G. E.; Thornback, J. R. *Inorg. Chim. Acta* **1981**, *56*, L41.
- (3) (a) Davison, A.; Orvig, C.; Trop, H. S.; Sohn, M.; DePamphilis, B. V.; Jones, A. G. *Inorg. Chem.* **1980**, *19*, 1988. (b) Cotton, F. A.; Davison, A.; Day, V. W.; Gage, L. D.; Trop, H. S. *Inorg. Chem.* **1979**, *18*, 3024.
- (4) Vanderheyden, J. L.; Ketring, A. R.; Libson, K.; Heeg, M. J.; Roecker, L.; Motz, P.; Whittle, R.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 3184.
- (5) Wester, D. W.; White, D. H.; Miller, F. W.; Dean, R. T. *Inorg. Chem.* **1984**, *23*, 1501.
- (6) Franklin, K. J.; Lock, C. J. L.; Sayer, B. F.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1982**, *104*, 5303.

- (7) Findeisen, M.; Kaden, L.; Lorenz, B.; Rummel, S.; Wahren, M. *Inorg. Chim. Acta.* **1987**, *128*, L15.
- (8) Griffith, J. S.; Orgel, L. E. *Trans. Faraday Soc.* **1957**, *53*, 601.
- (9) Minelli, M.; Enemark, J. H.; Brownlee, R. T. C.; O'Connor, M. J.; Wedd, A. G. *Coord. Chem. Rev.* **1985**, *68*, 169.
- (10) Dean, R. T.; Wester, D. W.; Nosco, D. L.; Adams, M. D.; Coveney, J. R.; Robbins, M. S.; McElvany, K. D.; deJong, R. In *Technetium in Chemistry and Nuclear Medicine*; Nicolini, M.; Bandoli, G.; Mazzi, U., Eds.; Cortina: New York, 1986; Vol. 2, p 147.

relative to pertechnetate. Since this shift is outside the expected range for Tc(I) species, we have remeasured the resonance frequency of $[\text{Tc}(\text{dmpe})_3]^+$ as well as the closely related species $[\text{Tc}(\text{P}(\text{OMe})_3)_6]^+$, also reported^{5,11} as being at an anomalously low field. On the basis of our studies, it was postulated that the resonances of diamagnetic Tc(I) complex should be close to those of the $[\text{Tc}(\text{CNR})_6]^+$ derivatives.

When a mixed sample of $(\text{NH}_4)[\text{TcO}_4]$ and $[\text{Tc}(\text{dmpe})_3](\text{PF}_6)$ was studied there was observed only the resonance attributable to pertechnetate in the region ± 500 ppm. A seven-line multiplet was observed, however, at a chemical shift of -1854 ppm. Indeed, when the spectrum (Figure 1) for a sample of $[\text{Tc}(\text{CNBu}^t)_6](\text{PF}_6)$ mixed with $[\text{Tc}(\text{dmpe})_3](\text{PF}_6)$ was obtained, resonances due to both species are observed. The technetium resonance at -1854 ppm, split by six equivalent phosphorus nuclei with $J_{\text{Tc-P}} = 574$ Hz, is clearly due to the $[\text{Tc}(\text{dmpe})_3]^+$ complex.¹² We also find the complex $[\text{Tc}(\text{P}(\text{OMe})_3)_6](\text{BPh}_4)$ to resonate at -1658 ppm as opposed to -422 ppm as previously reported.^{5,11} The coupling constant derived from the observed septet agrees within experimental error with the data obtained from the ^{31}P spectrum.^{13,14}

It is a common feature in the NMR of metal nuclei that the instrumentally imposed maximum spectral window is considerably smaller than the known chemical shift range. It seems probable that the previous workers have been measuring folded spectra that has led to their reporting incorrect chemical shifts. In all our measurements, careful consideration was given to this problem, and all spectra were obtained by using several different transmitter offsets.

If ^{99}Tc NMR is to be the useful tool for the study of technetium chemistry that we believe it to be, then it is essential that the chemical shifts for the already well-characterized species be known accurately.

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Registry No. $[\text{Tc}(\text{dmpe})_3](\text{PF}_6)$, 91491-92-8; $[\text{Tc}(\text{P}(\text{OMe})_3)_6](\text{BPh}_4)$, 97262-57-2; ^{99}Tc , 14133-76-7.

- (11) Wester, D. W.; White, D. H.; Miller, F. W.; Dean, R. T.; Schreifels, J. A.; Hunt, J. E. *Inorg. Chim. Acta.* **1987**, *131*, 163.
- (12) The same coupling constant was also observed by the previous workers.⁴
- (13) Abrams, M. J. Ph.D. Thesis, Massachusetts Institute of Technology, 1983.
- (14) The previous incorrect ^{99}Tc NMR studies^{5,11} reported the same coupling constants that we observed.

Contribution from the Dipartimento di Chimica and Dipartimento di Scienza della Terra, Sezione Cristallografia, Università di Perugia, 06100 Perugia, Italy

Synthesis and X-ray Structure of $\text{Cu}_2\text{L}_2(\text{CH}_3\text{COO})_2\cdot\text{Cu}_2(\text{CH}_3\text{COO})_4\cdot 2\text{C}_2\text{H}_5\text{OH}$ (LH = *N*-Methyl-*N'*-(4,6-dimethoxysalicylidene)-1,3-propanediamine), a Novel Alternating-Chain Compound of Copper(II)¹

B. Chiari, O. Piovesana,* T. Tarantelli, and P. F. Zanazzi

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Spin-spin interaction phenomena in cluster compounds and extended systems (a topic that is relevant to several areas of chemistry, physics, and biology) have been the object of several recent reviews.²

Many carboxylate complexes of copper(II) display structures in which exchange-coupled dimers with four Cu-O-C-O-Cu bridges are magnetically isolated from the bulk of the sample.³

* To whom correspondence should be addressed at the Dipartimento di Chimica.

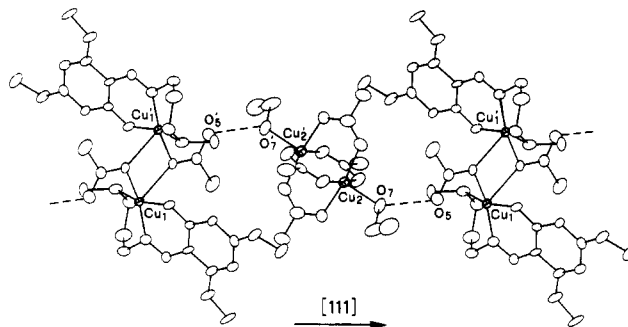


Figure 1. View of the 1-D chain structure of $\text{Cu}_2\text{L}_2(\text{CH}_3\text{COO})_2\cdot\text{Cu}_2(\text{C}_2\text{H}_5\text{COO})_4\cdot 2\text{C}_2\text{H}_5\text{OH}$. Hydrogen atoms have been omitted for clarity.

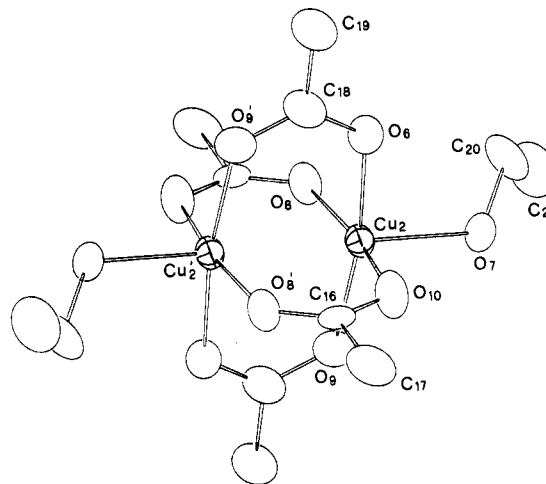


Figure 2. View of the $\text{Cu}_2(\text{CH}_3\text{COO})_4\cdot 2\text{C}_2\text{H}_5\text{OH}$ binuclear unit.

The intradimer spin coupling in these compounds is antiferromagnetic in nature, characterized by a singlet-triplet splitting ($-2J$) of about 300 cm^{-1} . Since 1951, more than 60 papers have appeared in the literature concerning the magnetic exchange problem for the copper acetate dimer,^{4,5} which has become a "reference" compound for discussing exchange concepts.

Intercluster exchange interactions are, in general, far more difficult to measure and interpret than intracluster exchange interactions. To our knowledge, only one compound involving binuclear copper acetate units, $\text{Cu}_2(\text{CH}_3\text{COO})_4$, has been designed for studying interdimer magnetic exchange, i.e. copper acetate-pyrazine.^{6,7} In this compound, the binuclear acetate units are linked by the bidentate pyrazine ligand, $\text{C}_4\text{H}_4\text{N}_2$, and a linear chain is formed.

We have recently investigated the structural and magnetic properties of several copper(II) compounds containing one-atom acetate-bridged Cu_2O_2 moieties.⁸⁻¹¹ Both structures built of

- (1) Exchange Interaction on Multinuclear Transition-Metal Complexes. 11. Part 10: Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1987**, *26*, 952.
- (2) See the various articles in: *Magneto-Structural Correlations in Exchange Coupled Systems*; Reidel: Dordrecht, 1985. Hatfield, W. E. *Comments Inorg. Chem.* **1981**, *1*, 105. Carlin, R. L.; De Jongh, L. J. *Chem. Rev.* **1986**, *86*, 659. Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834. Cairns, C. J.; Busch, D. H. *Coord. Chem. Rev.* **1986**, *69*, 1. O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203. Hatfield, W. E.; Estes, W. E.; Marsh, D. E.; Pickens, M. W.; ter Haar, L. W.; Weller, R. R. In *Extended Linear Chain Compounds*; Miller, J. S., Plenum: New York and London, 1983; Vol. 3, p 43. Willett, R. D.; Gaura, R. M.; Landee, C. P. *Ibid.*, p 143.
- (3) For reviews see: Doedens, R. J. *Prog. Inorg. Chem.* **1976**, *21*, 209. Melnic, M. *Coord. Chem. Rev.* **1982**, *42*, 259.
- (4) de Loth, P.; Cassoux, P.; Daudey, J. P.; Malrieux, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 407 and references therein.
- (5) Harcourt, R. D.; Skrezenek, F. L.; MacLagan, R. G. A. R. *J. Am. Chem. Soc.* **1986**, *108*, 5403 and references therein.
- (6) Valentine, J. S.; Silverstein, A. J.; Soos, Z. G. *J. Am. Chem. Soc.* **1974**, *96*, 97.
- (7) Morosin, B.; Hughes, R. C.; Soos, Z. G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 762.