

Short Note

Tetraethylammonium tribromo(triphenylphosphine)nickelate(II)

François Baril-Robert, Nicolas Bélanger-Desmarais and Christian Reber * 

Département de Chimie, Université de Montréal, Montréal, QC H3C 3J7, Canada; f.baril.robert@gmail.com (F.B.-R.); nicolas.belanger.desmarais@umontreal.ca (N.B.-D.)

* Correspondence: christian.reber@umontreal.ca

Abstract: The crystal structure and vibrational spectra of the tetraethylammonium salt of tribromotriphenylphosphinonickel(II) is reported. Br-Ni-Br angles vary between 108° and 121°, deviating from perfect tetrahedral angles.

Keywords: nickel(II) complexes; tetrahedral coordination; halide ligands

1. Introduction

Four-coordinate, approximately tetrahedral complexes of nickel(II) are widely used to illustrate magnetic and spectroscopic properties of these typical first-row compounds with the d^8 electron configuration [1,2]. Mixed ligand spheres are of particular interest and have given rise to detailed and illustrative analyses of different types of bonding and magnetic properties involving the highly degenerate electronic ground state [1,2]. Structural data and vibrational spectra are essential bases for such analyses. The structure of the tribromotriphenylphosphinenickel(II) anion, $[\text{NiBr}_3(\text{PPh}_3)]^-$ has been reported with the $[\text{Ph}_4\text{As}]^+$ counterion [3]. The structure of a trichloro analog was published in 2001 [4], decades later than [3], and with the tetraethylammonium counterion. We report here the structure of tetraethylammonium tribromo(triphenylphosphine)nickelate(II) in order to document structures for trichloro and tribromo anionic complexes with identical counterions and to determine deviations of Br-Ni-Br and Cl-Ni-Cl angles from those for perfect tetrahedral coordination. In addition, we report infrared (IR) and Raman spectra of the solid title compound (see Supplementary Materials), to complement the reported magnetic moments and electronic absorption data for the title compound and related four-coordinate nickel(II) complexes [5].

2. Results

The four-coordinate nickel(II) center in this structure shows approximately tetrahedral coordination geometry, as illustrated in Figure 1. The bromo ligands are disordered, also illustrated in the Figure.

The alkyl chains of the tetraethylammonium counterion are disordered, as reported for the chloro analog [4]. The X-Ni-X angles from the title compound, $[\text{NiBr}_3(\text{PPh}_3)][\text{Ph}_4\text{As}]$ [3] and $[\text{NiCl}_3(\text{PPh}_3)][\text{Et}_4\text{N}]$ [4] are summarized in Table 1.

Table 1. Br-Ni-Br and Cl-Ni-Cl angles for $[\text{NiBr}_3(\text{PPh}_3)]^-$ and $[\text{NiCl}_3(\text{PPh}_3)]^-$.

Compound	X-Ni-X [°]	X-Ni-X [°]	X-Ni-X [°]
$[\text{NiBr}_3(\text{PPh}_3)][\text{Et}_4\text{N}]^a$	110.6	113.2	117.0
$[\text{NiBr}_3(\text{PPh}_3)][\text{Ph}_4\text{As}]^b$	110.6	113.8	116.8
$[\text{NiCl}_3(\text{PPh}_3)][\text{Et}_4\text{N}]^c$	114.6	114.6	114.6

^a this work, ^b ref. [3], ^c ref. [4].



Citation: Baril-Robert, F.; Bélanger-Desmarais, N.; Reber, C. Tetraethylammonium tribromo(triphenylphosphine)nickelate(II). *Molbank* **2022**, *2022*, M1366. <https://doi.org/10.3390/M1366>

Academic Editor: Rodrigo Abonia

Received: 14 April 2022

Accepted: 7 May 2022

Published: 18 May 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

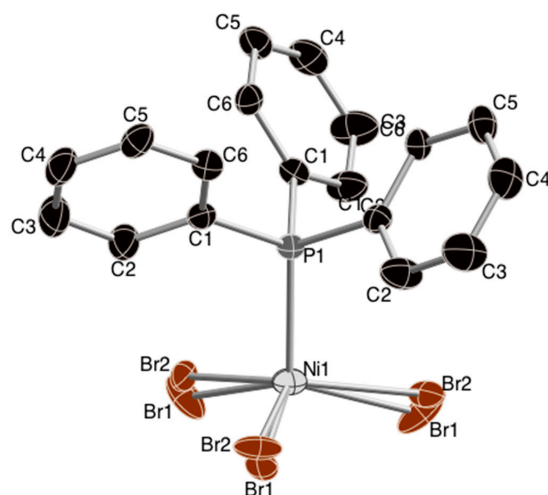


Figure 1. Structure of the $[\text{NiBr}_3(\text{PPh}_3)]^-$ anion with atom numbering. Hydrogen atoms are omitted for clarity. Ellipsoids for non-hydrogen atoms are shown at the 30% level.

The title compound shows Br-Ni-Br angles very similar to those published previously [3], wider than for perfect tetrahedral coordination by up to 8° . In contrast, the chloro analog [4] shows angles wider by 5° than for perfect tetrahedral structures. These deviations are relatively small and do not significantly affect the ligand-field electronic structure, where the most significant effects occur due to the differences in Ni-phosphine and Ni-halide bonding [1,2]. Full structural data are available at CCDC, deposition number 2166023.

The Raman and IR spectra of the crystalline title compound are shown in Figure 2. Peak positions are given in Table 2. Several, but not all vibrational transitions are observed both in IR and Raman spectra, as expected in perfect tetrahedral coordination geometry, showing therefore the close relationship of the title complex with idealized tetrahedral coordination geometry, despite the lower site symmetry for the nickel(II) ion in the title compound. Examples for such corresponding frequencies are the most intense Raman band at 3050 cm^{-1} and the corresponding IR peak at 3054 cm^{-1} , identical values within the precision and spectral resolution of the instruments used.

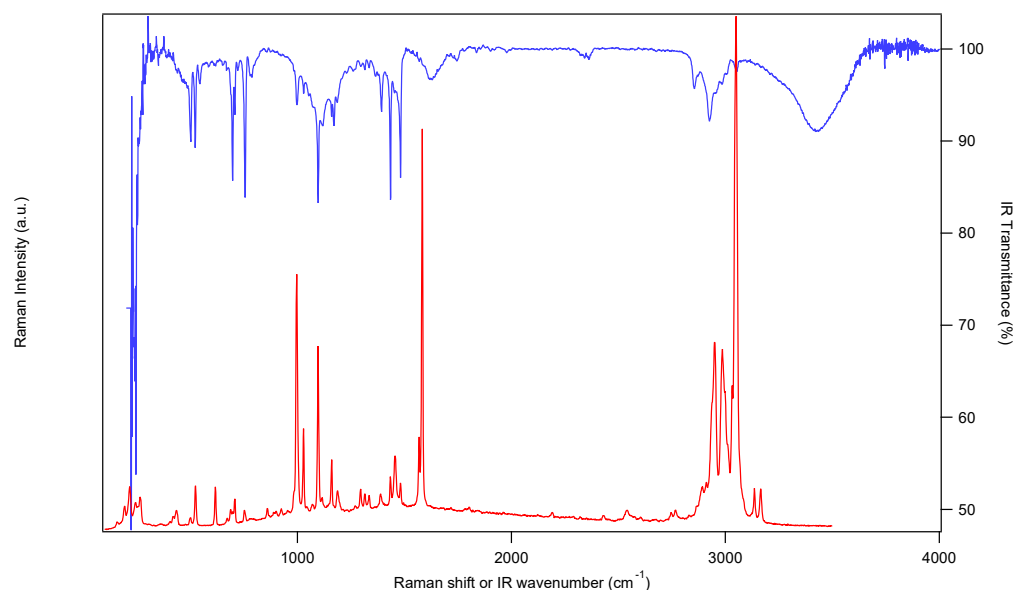


Figure 2. IR (blue, top trace) and Raman (red, bottom trace) spectra of (solid NEt_4)[$\text{NiBr}_3(\text{PPh}_3)$] recorded at room temperature.

Table 2. Observed peak positions in the IR and Raman spectra. All values in cm^{-1} units.

Raman Spectrum	Raman Spectrum (cont.)	IR Spectrum
157	1097 s	501
192	1116 w	523
216	1160	544
243	1296	697 s
264	1314	708
405	1335	755 s
419	1389	784 b
435	1434	998
500	1457	1029
524	1481	1098 s
617	1569	1118 b
672	1584 s	1160
688	2541 b	1171
698	2747 w	1393
707	2767 w	1435 s
751	2865 w	1482
761	2891 w	1620 b
890 b	2919 w	2855
901 b	2938	2925 b
925	2951	3054
954 w	2987 b	3430 s,b
996 s	3033	
1029	3050 s	
1071	3136	

s: strong, w: weak, b: broad.

3. Materials and Methods

(NEt_4) $\text{NiBr}_3(\text{PPh}_3)$ was crystallized from acetonitrile solutions of equivalent amounts of (NEt_4)Br and PPh_3 by adding a solution of anhydrous NiBr_2 dissolved in warm acetonitrile. We did not use reflux conditions, in contrast to the synthesis described in [6]. The solution was stirred for 1h, then filtered. Dark green crystals were obtained from solutions in a desiccator. Quantitative reaction yields were not determined. Crystals can be handled in the air briefly for spectroscopic measurements. The Raman spectrum was measured on a Renishaw Invia Raman microscope. The IR spectrum was recorded with a Bio-Rad Excalibur FTIR spectrometer with a CsI beamsplitter.

Supplementary Materials: The structure is available as CCDC 2166023, deposited 10 April 2022. The material can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (accessed on 7 May 2022).

Author Contributions: F.B.-R.: synthesis, X-ray diffraction, spectroscopic measurements N.B.-D.: structure analysis. C.R.: writing, figure with spectroscopic data. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Sciences and Engineering Research Council (Canada).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data for this study is available in this paper.

Acknowledgments: The authors thank Frank Schaper (Université de Montréal) for his invaluable help in the refinement of the structure, in particular with the disorder.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Davies, J.E.; Gerloch, M.; Phillips, D.J. Phosphine π -acceptor properties in dihalogenobis(triphenylphosphine)-nickel(II) and -cobalt(II). *J. Chem. Soc. Dalton Trans.* **1979**, 1836–1842. [[CrossRef](#)]
2. Gerloch, M.; Hanton, L.R. Donor and acceptor properties of triphenylphosphine ligands in trigonally distorted tetrahedral NiPX_3^- chromophores (X = bromine, iodine). *Inorg. Chem.* **1981**, *20*, 1046–1050. [[CrossRef](#)]
3. Hanton, L.R.; Raithby, P.R. Tetraphenylarsonium Tribromo(triphenylphosphine)nickelate(II). *Acta Cryst.* **1980**, *36*, 2417–2419. [[CrossRef](#)]
4. Smith, M.C.; Davies, S.C.; Hughes, D.L.; Evans, D.J. Tetraethylammonium trichloro(triphenylphosphine)nickelate(II). *Acta Cryst.* **2001**, *57*, m509–m510.
5. Sacconi, L.; Mani, F.; Bencini, A. Chapter 50 Nickel. In *Comprehensive Coordination Chemistry*, 1st ed.; Wilkinson, G., Gillard, R., McCleverty, J., Eds.; Pergamon Press: Oxford, UK; New York, NY, USA, 1987; Volume 5, p. 62.
6. Allender, G.; Smith, H.D. Five-Coordinate Ni(II) Complexes of 1,2-Bis(diphenylphosphino) o-carborane. *Inorg. Chim. Acta* **1978**, *26*, L38. [[CrossRef](#)]