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Synthesis and characterization of Bis (benzyltriphenylphosphonium) tetrachloromanganate (II) by using a Single crystal X-ray

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Abstract

Bis(benzyltriphenylphosphonium) tetrachloromanganate (II), a novel manganese(II) complex, was effectively synthesized and described in this work. Manganese (II) chloride and benzyltriphenylphosphonium chloride were directly reacted in a suitable solvent under carefully monitored conditions to create the complex. FT-IR, UV-Vis, and elemental analysis were among the spectroscopic and analytical methods used to examine the resultant crystalline compound. These methods confirmed that the Mn(II) center was coordinated with four chloride ligands in a tetrahedral geometry.

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تحضير وتشخيص ثنائي (بنزايل ثلاثي فنيل فوسفونيوم) رباعي كلورو منغنيز (II) باستخدام حيود الاشعة السينية للبلورة الأحادية

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جامعة الموصل، كلية التربية الأساسية، قسم العلوم، الموصل، العراق

المستخلص:

تم تحضير الملح العضوي بنزايل ثلاثي فنيل فوسفونيوم كلورايد من خلال التفاعل المباشر لكلوريد البنزيل مع ثلاثي فنيل فوسفين بنسبة واحد الى واحد لتكوين الملح العضوي ذو نقاوة عالية ومن ثم تحضير الملح المعقد له مع المنغنيز الثنائي من خلال تفاعل الملح العضوي المحضر مع كلوريد المنغنيز بنسبة اثنان الى واحد ومن ثم تشخيص الملح المعقد الناتج كبلورة نظامية باستخدام حيود الاشعة السينية للبلورة الأحادية والتقنيات الطيفية والفيزيائية الأخرى.

الكلمات المفتاحية: السوائل الايونية، الاملاح المعقدة، الاملاح المنصهرة.

Introduction:

The distinctive physicochemical characteristics of ionic liquids (ILs), which are salts that stay liquid at or close to room temperature, including their low vapor pressure, high thermal stability, broad electrochemical window, and superior solvating ability, have drawn increasing interest (Fabre & Murshed, 2021; T. Zhou et al., 2023). Phosphorus-based ionic liquids have become a particularly significant class of ionic liquids because of their improved chemical and thermal stability compared to conventional imidazolium or ammonium analogs. Greater hydrophobicity, adjustable viscosity, and resistance to decomposition in harsh environments are enabled by the bulky phosphonium cation (Li et al., 2024; X. Zhou et al., 2025).

Metal-containing ionic liquids (MILs) are created when metal ions or metal complexes are added to phosphonium ionic liquids to add new functions. These hybrid systems combine the advantageous solvent and transport characteristics of ionic liquids with the adaptable coordination chemistry of metals (Cui et al., 2024; Li et al., 2024). Metal-containing phosphonium ionic liquids are promising materials for catalysis, electrochemistry, materials synthesis, and separation processes because they can exhibit luminescence, redox behavior, magnetic properties, or catalytic activity, depending on the ligands and metal center characteristics (McCalmont et al., 2023; X. Zhou et al., 2025).

To attain the desired physical and chemical properties, recent research has focused on modifying the structures of the metal-containing anion and the phosphonium cation. Designing task-specific ionic liquids with improved performance and stability for industrial and environmental applications is enabled by the ability to fine-tune these systems at the molecular level (Abbas & Jung, 2024; Khazalpour et al., 2020; Xanthopoulos et al., 2019).

Experimental:

Preparation of complex salts benzyltriphenyl phosphonium tetrachloro manganate(II) **[$PhCH_2(PPh_3)_3P]_2[MnCl4]$**

(Ekstrom, 2022; Pérez et al., 2021; Saeed et al., 2025)

Concentrated HCl (1.0 ml) was added to a stirred solution of $MnCl_2 \cdot 4H_2O$ (1mmol) in MeCN (8 ml). After dissolving in MeCN (8 ml), benzotriphenylphosphonium chloride (1.00 g, 2.0 mmol) was added dropwise. A pale green crystalline solid separated after an hour of stirring at room temperature. $(Ph_3PCH_2Ph)_2[MnCl_4]$ was obtained as a green crystalline solid (yield: 88%) after the solid was collected by filtration, cleaned with cold diethyl ether (2 × 5 ml), and dried under reduced pressure. Slow vapor diffusion of diethyl ether into an acetonitrile solution of the product yielded single crystals suitable for X-ray diffraction.

The formation of distinct ionic units comprising two $(Ph_3PCH_2Ph)^+$ cations and a central $[MnCl_4]^{2-}$ anion was revealed by the single-crystal X-ray diffraction study, which also provided detailed structural information. Strong ionic interactions between cations and anions within the lattice were demonstrated by the crystallographic data, which also validated the complex's tetrahedral geometry around the Mn(II) ion.

A Bruker D8 diffractometer equipped with an APEX CCD detector and 1.5 kW graphite-monochromated Mo radiation was used to collect single-crystal X-ray data. The distance between the detector and the crystal was 5.985 cm. Throughout the data collection process, scan widths of 0.3º and exposure times of 10 s per frame were employed. For a numerical absorption correction, the crystal's faces were indexed, and their separations from the center were measured. Three ω scans with varying φ values were used to collect the data, and the results showed an average completeness of 92.1-97.9% and ranged from 2.23 to 33.44 °. The SAINT vv7.4a5a (1500) was integrated with the frames. X-SEED, a graphical user interface for SHELX, was used to solve and refine the structure.

The structural characteristics of phosphonium-based manganese complexes have been improved upon through this work, which could be helpful for future coordination chemistry and materials science research.

Result and discussions:

There have been numerous attempts to produce appropriate crystals for most complex salts, but most have failed, yielding only tiny crystals or an amorphous state .

Compound **$[PhCH_2(PPh_3)_3P]_2[MnCl_4]$** crystallizes in the monoclinic space group C2/c with four formula unit cells, forming dark olive crystals. Two **$[PhCH_2(PPh_3)_3P]^+$** cations and one **$[MnCl_4]^{-2}$** anion make up the asymmetric unit.

Around the Mn(II) center, the metal-containing anion **$[MnCl_4]^{-2}$** has a tetrahedral geometry. The layer plane is formed by these anions, which are positioned between the benzotrizolium rings. As an alternative, the entire structure may be viewed as being composed of ID chains made up of the **$[PhCH_2(PPh_3)_3P]^+$** cation and the **$[MnCl_4]^{-2}$** anion, which are connected by intermolecular hydrogen bonds.

Every bond length and bond angle falls within the typical range and is comparable to values reported in the literature (Saeed et al., 2025; Ye et al., 2016).

The following tables and figures contain the data for the identified crystal.

OpenGL version: 4.6.0 - Build 30.0.101.1122

Video configuration: Intel(R) UHD Graphics

Maximum supported width and height of the viewport: 16384 x 16384

OpenGL depth buffer bit: 16

[PhCH2(PPh3)3P]2[MnCl4]

Lattice type P

Space group name P 21/c

Space group number 14

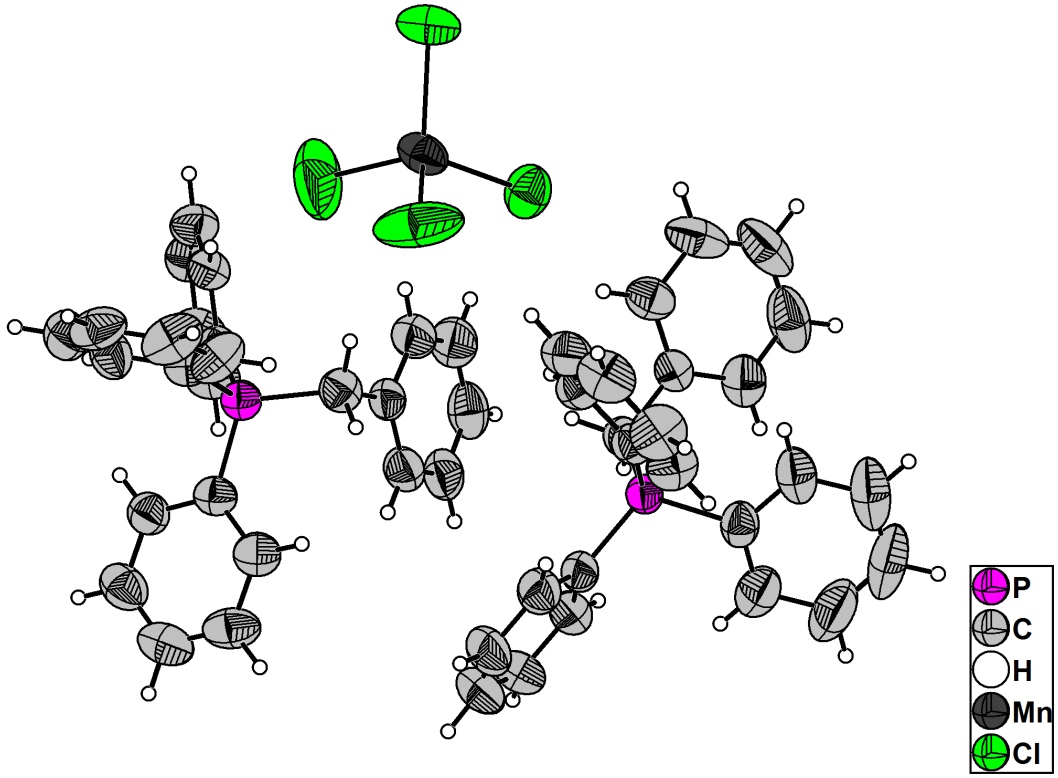

Fig (1): Compound $[PhCH_2(PPh_3)_3P]_2[MnCl4]$ crystal structure

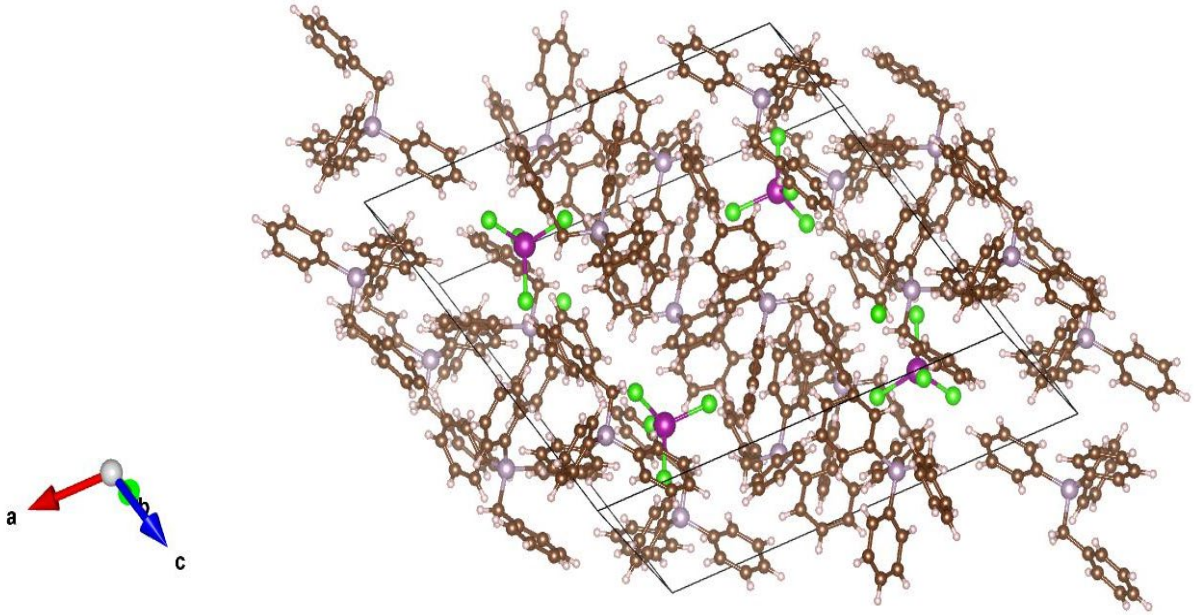

Fig (2): The unit cell of compound $[PhCH_2(PPh_3)_3P]_2[MnCl4]$

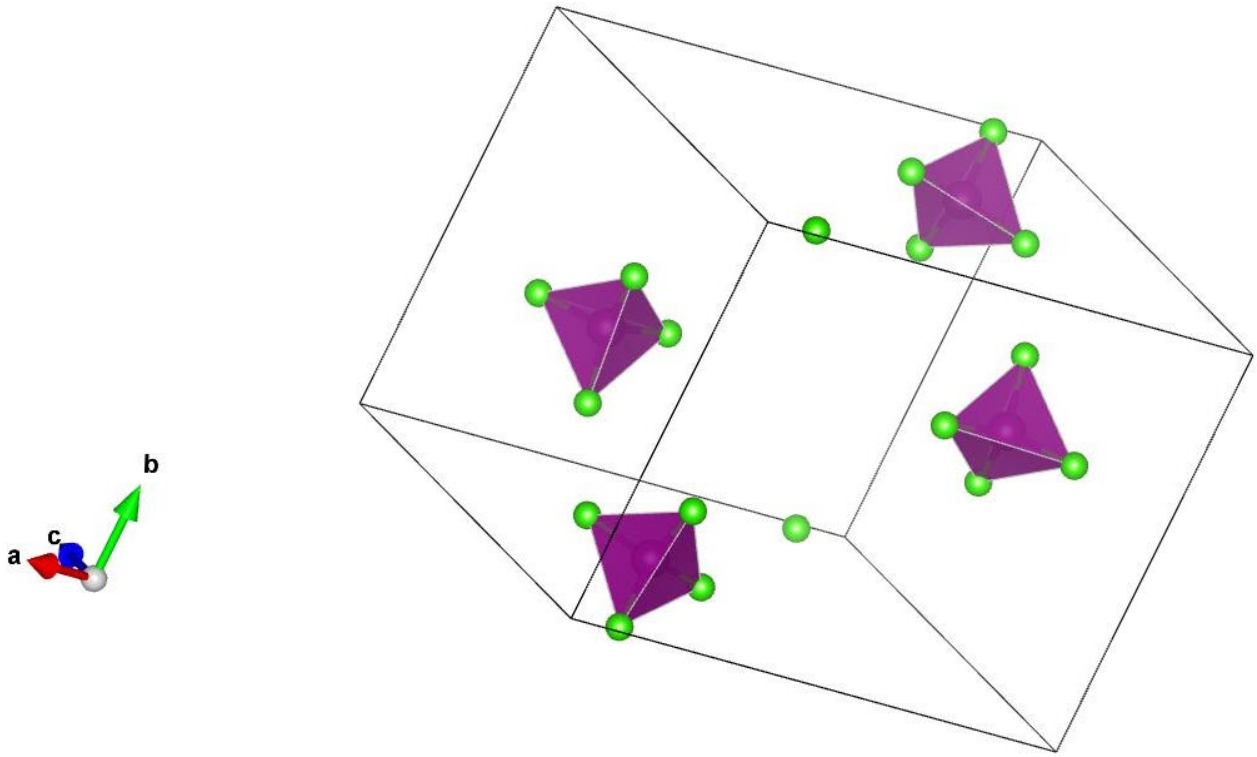

Fig (3): The unit cell of the [MnCl4]-2 polyhedron shape

Table (1): Crystal data of compound $[PhCH_2(PPh_3)_3P]_2[MnCl4]$

Empirical formula	2(C25 H22 P), Cl4 Mn
Formula weight	904
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 21.59500 (8) Å α = 90° b = 12.63200 (6) Å β = 114.25 (10)° c = 18.55400 (14) Å γ = 90°
Z	4

Table (2): Hydrogen coordinates (x 104) and isotropic displacement parameters (Å2 x 103) of compound $[PhCH_2(PPh_3)_3P]_2[MnCl4]$

No.	Atom	Sym.	x	y	z	Occ.	U	Site	Sym.
1	P	P03	0.12149	0.02537	0.16744	1	0.05	4e	1
2	C	C021	0.1778	0.0696	0.331	1	0.05	4e	1
3	C	C022	0.1541	-0.0242	0.099	1	0.055	4e	1
4	C	C3	0.1934	0.0365	0.262	1	0.053	4e	1
5	H	H3A	0.21629	-0.03141	0.27443	1	0.063	4e	1
6	H	H3B	0.22494	0.08733	0.25673	1	0.063	4e	1
7	C	C023	0.1533	-0.0045	0.369	1	0.071	4e	1
8	H	H023	0.14539	-0.07409	0.35109	1	0.085	4e	1
9	C	C028	0.1193	0.2437	0.1515	1	0.064	4e	1
10	H	H028	0.16506	0.24219	0.1856	1	0.077	4e	1
11	C	C031	0.0815	0.1506	0.1324	1	0.056	4e	1
12	C	C042	0.1376	0.025	0.0266	1	0.069	4e	1
13	H	H042	0.10908	0.08368	0.01272	1	0.083	4e	1
14	C	C047	0.1959	-0.1132	0.1186	1	0.069	4e	1
15	H	H047	0.20663	-0.14741	0.16663	1	0.083	4e	1
16	C	C8	0.018	-0.2374	0.1786	1	0.118	4e	1
17	H	H8	0.01769	-0.30925	0.16764	1	0.142	4e	1
18	C	C058	0.1902	0.1731	0.3589	1	0.066	4e	1
19	H	H058	0.20713	0.22246	0.33445	1	0.08	4e	1
20	C	C064	0.0878	0.3392	0.1189	1	0.077	4e	1
21	H	H064	0.11255	0.40192	0.13223	1	0.093	4e	1
22	C	C065	0.0164	-0.0233	0.2089	1	0.08	4e	1
23	H	H065	0.0161	0.04869	0.21933	1	0.095	4e	1
24	C	C067	0.1642	-0.0139	-0.0252	1	0.086	4e	1
25	H	H067	0.15412	0.01988	-0.07326	1	0.104	4e	1
26	C	C081	0.2215	-0.1503	0.0654	1	0.086	4e	1
27	H	H081	0.25012	-0.20882	0.07832	1	0.103	4e	1
28	C	C083	-0.0161	0.2493	0.0479	1	0.093	4e	1
29	H	H083	-0.06152	0.25115	0.0123	1	0.112	4e	1
30	C	C084	0.0618	-0.1693	0.1629	1	0.079	4e	1
31	H	H084	0.09184	-0.19575	0.14295	1	0.095	4e	1
32	C	C085	-0.0263	-0.0905	0.2248	1	0.105	4e	1
33	H	H085	-0.05621	-0.06449	0.2451	1	0.127	4e	1

No.	Atom	Sym.	x	y	z	Occ.	U	Site	Sym.
34	C	C087	0.0602	-0.0619	0.1772	1	0.058	4e	1
35	C	C089	0.1411	0.0266	0.4334	1	0.099	4e	1
36	H	H089	0.12524	-0.0223	0.45931	1	0.118	4e	1
37	C	C093	0.1524	0.131	0.4595	1	0.103	4e	1
38	H	H093	0.14291	0.15192	0.50203	1	0.123	4e	1
39	C	C097	0.2044	-0.1003	-0.0059	1	0.093	4e	1
40	H	H097	0.22078	-0.12656	-0.04154	1	0.112	4e	1
41	C	C100	0.0209	0.3411	0.0676	1	0.088	4e	1
42	H	H100	0.00032	0.40507	0.04602	1	0.106	4e	1
43	C	C101	-0.0243	-0.1982	0.2101	1	0.119	4e	1
44	H	H101	-0.05228	-0.24437	0.22202	1	0.142	4e	1
45	C	C102	0.1771	0.2026	0.4235	1	0.089	4e	1
46	H	H102	0.18528	0.27179	0.44217	1	0.107	4e	1
47	C	C107	0.0134	0.1546	0.0803	1	0.076	4e	1
48	H	H107	-0.01226	0.09283	0.0674	1	0.092	4e	1
49	P	P05	0.39929	0.33146	0.13143	1	0.051	4e	1
50	C	C015	0.3577	0.1726	0.0171	1	0.063	4e	1
51	H	H015	0.31487	0.17881	0.01728	1	0.076	4e	1
52	C	C017	0.3383	0.2152	0.2106	1	0.055	4e	1
53	C	C018	0.4118	0.2326	0.0694	1	0.052	4e	1
54	C	C020	0.3891	0.4551	0.0806	1	0.057	4e	1
55	C	C032	0.4832	0.4317	0.2669	1	0.06	4e	1
56	H	H032	0.45478	0.48969	0.2466	1	0.072	4e	1
57	C	C036	0.3377	0.1085	0.1907	1	0.064	4e	1
58	H	H036	0.32712	0.08939	0.13855	1	0.078	4e	1
59	C	C038	0.3517	0.2411	0.2875	1	0.07	4e	1
60	H	H038	0.35057	0.31155	0.3014	1	0.084	4e	1
61	C	C041	0.4748	0.2222	0.0668	1	0.06	4e	1
62	H	H041	0.51146	0.26145	0.10129	1	0.072	4e	1
63	C	C046	0.4453	0.5018	0.0752	1	0.07	4e	1
64	H	H046	0.48816	0.47238	0.10235	1	0.084	4e	1
65	C	C048	0.3526	0.032	0.2475	1	0.074	4e	1
66	H	H048	0.35263	-0.03895	0.23402	1	0.088	4e	1
67	C	C053	0.3681	0.1032	-0.0355	1	0.077	4e	1
68	H	H053	0.33218	0.06246	-0.06963	1	0.092	4e	1

No.	Atom	Sym.	x	y	z	Occ.	U	Site	Sym.
69	C	C056	0.5156	0.2544	0.254	1	0.069	4e	1
70	H	H056	0.50876	0.19221	0.22489	1	0.083	4e	1
71	C	C061	0.5799	0.3545	0.3694	1	0.07	4e	1
72	H	H061	0.61658	0.35982	0.41832	1	0.084	4e	1
73	C	C063	0.3249	0.3033	0.1504	1	0.061	4e	1
74	H	H06A	0.31163	0.36685	0.16982	1	0.073	4e	1
75	H	H06B	0.28761	0.283	0.1014	1	0.073	4e	1
76	C	C066	0.4304	0.0948	-0.0371	1	0.078	4e	1
77	H	H066	0.43685	0.04869	-0.07254	1	0.094	4e	1
78	C	C068	0.5376	0.4377	0.3411	1	0.07	4e	1
79	H	H068	0.54468	0.49919	0.37099	1	0.084	4e	1
80	C	C069	0.3199	0.5921	-0.0045	1	0.087	4e	1
81	H	H069	0.27757	0.62318	-0.03142	1	0.104	4e	1
82	C	C070	0.4838	0.1544	0.0137	1	0.074	4e	1
83	H	H070	0.52618	0.14894	0.01213	1	0.089	4e	1
84	C	C074	0.3261	0.5023	0.0406	1	0.078	4e	1
85	H	H074	0.28789	0.47338	0.04425	1	0.094	4e	1
86	C	C076	0.3669	0.1628	0.3445	1	0.082	4e	1
87	H	H076	0.37677	0.18124	0.39656	1	0.099	4e	1
88	C	C079	0.3753	0.6345	-0.0096	1	0.084	4e	1
89	H	H079	0.37051	0.69432	-0.0407	1	0.1	4e	1
90	C	C082	0.3676	0.06	0.3249	1	0.075	4e	1
91	H	H082	0.37812	0.00792	0.36357	1	0.09	4e	1
92	C	C086	0.4721	0.3387	0.2239	1	0.053	4e	1
93	C	C106	0.5695	0.262	0.3272	1	0.08	4e	1
94	H	H106	0.59852	0.20482	0.34769	1	0.096	4e	1
95	C	C108	0.4383	0.5914	0.0301	1	0.079	4e	1
96	H	H108	0.47608	0.6222	0.02673	1	0.094	4e	1
97	Mn	Mn02	0.23428	0.59384	0.25015	1	0.071	4e	1
98	Cl	Cl	0.34539	0.5656	0.2615	1	0.173	4e	1
99	Cl	Cl1	0.15786	0.60542	0.11634	1	0.154	4e	1
100	Cl	Cl2	0.22966	0.7488	0.31777	1	0.093	4e	1
101	Cl	Cl3	0.20671	0.44366	0.30697	1	0.081	4e	1

According to the supporting data file and the crystal data file, the exact chemical composition was ascertained by employing the proper instrument for X-ray diffraction of the single crystal (Chen et al., 2012; De Bruycker et al., 2016; Hafiz, 2008).

Conclusions:

A straightforward metathesis reaction between benzyltriphenylphosphonium chloride and manganese(II) chloride in a chloride-rich medium yielded the complex salt bis (benzyltriphenylphosphonium) tetrachloro manganate(II). The tetrachloromanganate (II) anion could be incorporated into a stable ionic framework by the use of phosphonium cations. The target complex was confirmed to have formed when the resultant compound displayed the anticipated spectroscopic and physical characteristics. This synthesis demonstrates that metal-containing phosphonium ionic complexes, which can serve as useful precursors or functional materials in coordination chemistry and ionic liquid research, can be produced using an effective, simple method.

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